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Initial Sampling Plan for the Reilly Tar & Chemical Corp.

N.P.L. Site

St. Louis Park, Minnesota

October 4, 1986

Amended January 1987

Prepared for:

City of St. Louis Park
St. Louis Park, Minnesota

February 1987

ERT

A RESOURCE ENGINEERING COMPANY

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CONTENTS

Section A	Site Management Plan
Section B	Quality Assurance Project Plan
Section C	Health & Safety Plan
Section D	Community Relations Plan

SECTION A

/ SITE MANAGEMENT PLAN

INTRODUCTION

Ground water in the City of St. Louis Park, Minnesota has been contaminated by activities at a coal-tar distillation and wood preserving plant operated from 1917 to 1972. Numerous previous studies have identified polynuclear aromatic hydrocarbons (PAH) present in various aquifers beneath St. Louis Park and adjacent communities.

The United States Environmental Protection Agency (EPA), the Minnesota Pollution Control Authority (MPCA), the Minnesota Department of Health (MDH), the City of St. Louis Park (SLP), and Reilly Tar & Chemical Corporation (Reilly) have agreed to acceptable water quality criteria for PAH. These criteria, as incorporated into the Consent Decree, include the following concentration levels:

	<u>Advisory Level</u>	<u>Drinking Water Criteria</u>
o Sum of benzo(a) pyrene and dibenz(a,h) anthracene	3.0 ng/l*	5.6 ng/l
o Carcinogenic PAH	15 ng/l	28 ng/l
o Other PAH	175 ng/l	280 ng/l

*or the lowest concentration that can be quantified, whichever is greater

In conjunction with the implementation of remedial measures to limit the spread of contaminants, a granular activated carbon (GAC) treatment system has been installed to treat water from St. Louis Park (SLP) wells 10 and 15. Further provisions of the Remedial Action Plan (RAP) call for long-term monitoring of the influent and effluent of the GAC treatment plant and the major aquifers underlying the region. The general objective of the monitoring program is to identify the distribution of PAH and/or phenolics in the ground water. The analytical data will be used to evaluate contamination by comparing the levels of PAH and/or phenolics found in the various samples with historical water quality data and with water quality criteria established in the Consent Decree-RAP. The specific objectives of the sampling and analysis program, and therefore, the intended end use of the data vary slightly for the different aquifers being monitored in accordance with the Consent Decree-RAP.

The GAC plant monitoring is being done to assess and continuously evaluate the performance of the treatment system. Analytical results for influent and effluent samples will be compared to the drinking water criteria for PAH as established in the Consent Decree-RAP. Based on these

comparisons, decisions will be made on: 1) possible modifications to the treatment system (e.g., adding another carbon column), 2) system operations (e.g., when the carbon should be replaced), and 3) cessation of the treatment system, if desired, when sufficiently low concentrations of PAH in influent samples are demonstrated.

The objective of sampling the four existing Mt. Simon-Hinckley Aquifer municipal drinking water wells and any new Mt. Simon-Hinckley Aquifer municipal drinking water wells installed within one mile of well W23, and analyzing for PAH, is to assure the continued protection of these wells from PAH resulting from activities of Reilly at the site. The analytical data will be used to make comparisons between the levels of PAH found in the Mt. Simon-Hinckley Aquifer, and the drinking water criteria established in the Consent Decree-RAP.

The objective of sampling and analyzing the Ironton-Galesville Aquifer source control well (W105) is to assess the levels of PAH in the discharge from W105 when it is pumping a monthly average of 25 gallons per minute. The data will be used to compare the concentration of total PAH in the samples to a cessation criterion of 10 micrograms per liter of total PAH established in the Consent Decree-RAP. Also, if any new Ironton-Galesville Aquifer drinking water wells are installed within one mile of well W23, then those wells will be sampled and analyzed for PAH to meet the objective of assuring protection of the well from PAH resulting from the activities of Reilly at the site. The analytical data would be used to compare the levels of PAH found in potential Ironton-Galesville Aquifer drinking water wells to the drinking water criteria established in the Consent Decree-RAP.

The objectives of monitoring the many Prairie du Chien-Jordan Aquifer wells, including municipal drinking water wells, private or industrial wells, and monitoring wells are to: 1) monitor the distribution of PAH in the aquifer, thus evaluating the source and gradient control systems, and 2) assure the continued protection of drinking water wells from PAH resulting from the activities of Reilly at the site. The analytical data will be used to compare the levels of PAH in the Prairie du Chien-Jordan aquifer to historical PAH data and to various criteria established in the Consent Decree-RAP (e.g., drinking water criteria for drinking water wells, and a cessation criterion of 10 micrograms per liter of total PAH for source control well W23). Analytical data for samples of the discharge from gradient control well SLP4 will be compared to discharge limitations in an NPDES permit that will be applied for at the conclusion of a Feasibility Study to determine the appropriate disposition of SLP4 discharge. Water level data will be used to evaluate ground-water flow patterns in the Prairie du Chien-Jordan Aquifer.

The objective of monitoring St. Peter Aquifer wells is to determine the nature and extent of PAH in the St. Peter Aquifer resulting from the activities of Reilly at the site. The analytical data will

be used to compare the levels of PAH in the St. Peter Aquifer to historical PAH data and to the drinking water criteria established in the Consent Decree-RAP. Water level data will be used to evaluate ground-water flow patterns in the St. Peter Aquifer.

The objectives of monitoring the Drift-Platteville Aquifer wells are to: 1) monitor the distribution of PAH and phenolics in the aquifer, thus evaluating the source and gradient control systems, and 2) to further define the nature and extent of PAH and phenolics in the Northern Area of the Drift-Platteville Aquifer resulting from the activities of Reilly at the site. The analytical data will be used to compare levels of PAH and phenolics in the Drift-Platteville Aquifer with historical water quality data for the aquifer and with various criteria established in the Consent Decree-RAP for PAH and phenolics. Water level data will be used to evaluate ground-water flow patterns in the Drift-Platteville Aquifer.

This Site Management Plan outlines the scope of work to be performed in order to monitor the ground water in the St. Louis Park, MN area in accordance with the Consent Decree - RAP related to the Reilly Tar & Chemical Corp. N.P.L. site. Included in this plan are: 1) the identity of wells to be monitored, 2) the schedule for ground-water monitoring, and 3) a description of the procedures that will be used for sample collection, water level measurement, sample handling, sample analysis, and reporting.

The time period covered by the Initial Sampling Plan is from the date of its acceptance and approval by the agencies, to December 31, 1987. This is one year longer than the initial Plan is required to cover as stated in the RAP (section 3). The reason for this change is that, according to the schedule in the RAP, a Sampling Plan for 1987 would be due before comments were received on the Initial Sampling Plan. Therefore, to avoid that situation, and to present a clear picture of ground-water monitoring activities through the first year of monitoring, this Plan covers sampling through the 1987 calendar year. The first subsequent Sampling Plan (RAP section 3.3) will be submitted by October 31, 1987, covering the 1988 calendar year.

This Plan incorporates the requirements of RAP Sections 3.2, 3.3, 4.3, 5.1, 6.1.4, 7.3, 8.1.3, 9.1.3, 9.2.3, 9.3.3, and 9.6. Some of the sampling required under RAP Section 4.3 (Monitoring the GAC System) has already taken place prior to the Effective Date. Therefore, only the monitoring that will take place from the approval date of this Initial Sampling Plan through December 31, 1987 is included in this Plan.

SAMPLING SCHEDULE

The actual dates of ground-water monitoring are based on the timing of activities conducted under the RAP, and these dates cannot be predicted now with certainty. For example, except for the interim monitoring of the GAC plant, no monitoring will take place until this plan is approved. Therefore, the proposed sampling schedule outlined in this sampling plan indicates the starting criteria and the frequencies of sampling as outlined in the RAP to determine when the wells are sampled (Tables 1 and 2). In general, the sampling schedule will be constructed to allow economies of scale in the field and in the laboratory by grouping the various monitoring events described by the RAP as much as possible. Samples will be collected within the time periods indicated on Tables 1 and 2.

Tables 1 and 2 summarize the ground-water monitoring schedule for the period through December 1987. Table 2 includes monitoring schedules for wells that have not been built yet (e.g., five new St. Peter Aquifer monitoring wells, RAP Section 8.1.3; six new Drift-Platteville Aquifer monitoring wells, RAP Section 9.3.3; and three new Drift-Platteville Aquifer source and gradient control wells, RAP Section 9.3.2) and for wells that have not been retrofitted for long-term pumping (e.g., wells W23 and W105). The monitoring of these wells will begin during the sampling period covered in this plan, but the exact time is not certain. Subsequent progress reports, which are required under Part K of the Consent Decree, should be relied upon to provide better information on sampling dates for these wells. Also, all parties will be given two weeks notice in advance of routine sampling.

The sampling schedule outlined in Tables 1 and 2 represents the minimum monitoring program that is likely to occur during the year. However, additional sampling will take place if treated water from the GAC plant or ground-water from active municipal drinking water wells exceeds the drinking water criteria established in the Consent Decree-RAP. This additional sampling is described in Sections 4 and 12 of the RAP, and are reproduced in Appendix A of this Site Management Plan.

The duration of field sampling events will depend on the number and type of wells to be sampled. For estimating purposes, it is assumed that between 10 and 20 active pumping wells (e.g., municipal, industrial, or gradient/source control wells), and between 4 and 8 monitoring wells can be sampled in one day. It is a reasonable expectation that most sampling events will take place over the better part of a week, and some sampling may be done over a longer time frame.

**TABLE 1. INITIAL SAMPLING PLAN GAC PLANT
MONITORING SCHEDULE ^(a)**

<u>RAP Section</u>	<u>Sampling Points</u>	<u>Start of Monitoring</u>	<u>Sampling Frequency</u>	<u>Analyses</u> ^(b)
4.3.1 (C)	Treated water(TRTD)	Date of plan approval	Monthly	PAH(ppt) ^(c)
4.3.3 (C)	Feed water(FEED)	Date of plan approval	Quarterly	PAH(ppt)
4.3.4	Treated water	Date of plan approval	Annually	Extended PAH(ppt)
4.3.4	Treated or Feed water	Date of plan approval	Annually	Acid fraction compounds in EPA Test Method 625.

(a) This schedule does not include certain contingencies (eg. exceedance monitoring) and, therefore, represents the minimum program that is likely to occur between the date this Plan is approved and December 31, 1987. Sections 4 and 12 of the RAP outline the additional sampling that will be conducted if PAH criteria are exceeded. The first samples will be collected during the period indicated by the monitoring frequency following the date of the start of monitoring. The location of the GAC plant is shown in Figure 1.

(b) Lists of parameters and methods for analysis of PAH, extended PAH, and acid fraction compounds in EPA Test Method 625 are provided in the QAPP. Field blanks will be collected and analyzed at a frequency of one per day. Duplicate samples will be collected and analyzed at a frequency of one per 10 samples.

(c) ppt = parts per trillion. This signifies analysis using selected ion monitoring gas chromatography mass spectrometry.

**TABLE 2. INITIAL SAMPLING PLAN GROUND-
WATER MONITORING SCHEDULE ^(a)**

<u>Source of Water</u>	<u>RAP Section</u>	<u>Sampling^(l) Points</u>	<u>Start of Monitoring</u>	<u>Sampling Frequency</u>	<u>Analyses^(b)</u>
Mt. Simon-Hinckley Aquifer	5.1	SLP11, SLP12, SLP13, SLP17	Within six months of Effective date ^(g)	Annually	PAH (ppt) ^(c)
	5.3.2	New municipal wells within one mile of well W23	At the time of installation	Annually	PAH(ppt)
Ironton-Galesville Aquifer	6.1.4	W105 W38 ^(e)	Start of pumping	Quarterly	PAH (ppb) ^(d)
	6.2.1	New municipal wells within one mile of well W23	At the time of installation	Annually	PAH(ppt)
Prairie du Chien-Jordan Aquifer	7.3 (A)	SLP4	Start of pumping	Quarterly	PAH (ppt) ^(h) phenolics
	7.3 (B)	W23	Start of pumping	Quarterly	PAH (ppb)
	7.3 (C)	SLP6, SLP7 or SLP9, W48	Date of plan approval	Quarterly	PAH (ppt)
	7.3 (D) ^(m)	AHM or MGC ⁽ⁱ⁾ , E2, E13, H3, SLP10 or SLP15, SLP14, SLP16, W402 ^(j) W403, W119	Date of plan approval	Semi-annually	PAH (ppt)
	7.3 (E) ^(m)	SLP5, H6, E3, E15, MTK6, W29, W40, W70, W401 ^(j)	Date of plan approval	Annually	PAH (ppt)
	7.3 (F)	W112, W32, SLP8, SLP10, E4, E7	Date of plan approval	Quarterly	No chemical analyses ^(f)
St. Peter Aquifer	8.1.3	SLP3, W14, W24, W33, W122, W129 W133, P116, plus 5 new wells	Within 30 days of installing new wells	Once	PAH (ppt)
		SLP3 plus six of the wells listed above ⁽ⁿ⁾	Within 6 months of above	Once	PAH (ppt)

TABLE 2 (continued)

<u>Source of Water</u>	<u>RAP Section</u>	<u>Sampling^(l) Points</u>	<u>Start of Monitoring</u>	<u>Monitoring Frequency</u>	<u>Analyses^(b)</u>
Drift-Platteville Aquifer	9.1.3 and 9.2.3	Source and gradient control wells (3 wells)	Start of pumping	Quarterly	PAH (ppb) and total phenols
	9.3.3	W131, W136, plus 6 new wells	Within 30 days of well installations	Once	Expanded analysis
	9.3.3	W131, W136 plus 6 new wells	Within 6 months of above	Once	PAH(ppb) and total phenols
	9.6	Drift: W2, W5, W15, W11, W12, W16, W116, W117, W128, W135, W136, PB140; Platteville: W1, W19, W20, W22, W115, W120, W121, W123, W130, W131, W132, W143, plus 6 new wells	Concurrent ^(k) with 9.3.3 sampling	Concurrent ^(k) with 9.3.3 sampling	PAH (ppb) and total phenols

- (a) This schedule does not include certain contingencies (eg. exceedance monitoring) and, therefore, represents the minimum program that is likely to occur between the date this Plan is approved and December 31, 1987. Section 12 of the RAP outlines the additional sampling that will be conducted if the drinking water criteria are exceeded in samples from water supply wells. The first samples will be collected during the period indicated by the monitoring frequency following the date of the start of monitoring. Field blanks will be collected at a frequency of one per day, and one duplicate sample will be collected for every 10 samples.
- (b) Lists of parameters and descriptions of the methods for analysis of PAH, phenolics, and expanded analyses are provided in the QAPP. Water levels will be measured each time samples are collected for analysis, except for those wells which prove to be inaccessible for such measurements.
- (c) ppt = parts per trillion. This signifies analysis using selected ion monitoring gas chromatography mass spectrometry.
- (d) ppb = parts per billion. This signifies analysis by EPA Method 625. If analytical results for individual wells are below 20 micrograms per liter (20 ppb) using this method, then the part per trillion method will be used on subsequent monitoring rounds.
- (e) Water levels in W38 will be measured each time W105 is sampled.
- (f) Water levels only (no monitoring) will be measured at these wells, except for those wells which prove to be inaccessible for such measurements.

TABLE 2 (continued)

- (g) Or within 30 days of the approval date of this Plan, whichever is later.
- (h) SLP4 analytical program will be determined by the results of the Feasibility Study.
- (i) AHM = American Hardware Mutual, MGC = Minikahda Golf Course.
- (j) Wells W401, W402, and W403 may or may not be available for sampling at the same time as the other wells on these lists. They will be sampled in conjunction with the monitoring performed in accordance with the schedule shown, once they are available for sampling.
- (k) If the six new Drift-Platteville Aquifer monitoring wells have not been installed by the appropriate time, then monitoring of the wells listed here will be done semi-annually for the first year following the effective date. There will be other opportunities for concurrent sampling. If the six new Drift-Platteville Aquifer monitoring wells are available for concurrent sampling, then the following eight wells will be omitted from the first sampling round, due to the Regional Administrator and Director's request for the eight expanded analysis as shown for RAP Section 9.3.3: W1, W2, W22, W116, W123, W128, W130, and PB140.
- If any of the wells listed here become damaged, destroyed, or otherwise unsuitable for sampling, alternate wells will be selected by the Project Leaders for monitoring.
- (l) Sampling points are located on the maps shown in Figures 1 through 5. Letter prefixes to well codes are defined as follows:
- | | |
|-----|------------------------------|
| W | - 4-inch monitoring well |
| P | - monitoring piezometer |
| PB | - 2-inch monitoring well |
| SLP | - St. Louis Park supply well |
| E | - Edina supply well |
| H | - Hopkins supply well |
| MTK | - Minnetonka supply well |
- (m) Water level measurements will be made quarterly at these wells, except for those wells which prove to be inaccessible for such measurements.
- (n) The six St. Peter Aquifer monitoring wells that will be monitored according to RAP Section 8.1.3 will be selected by the Project Leaders based on the results of the first monitoring round.

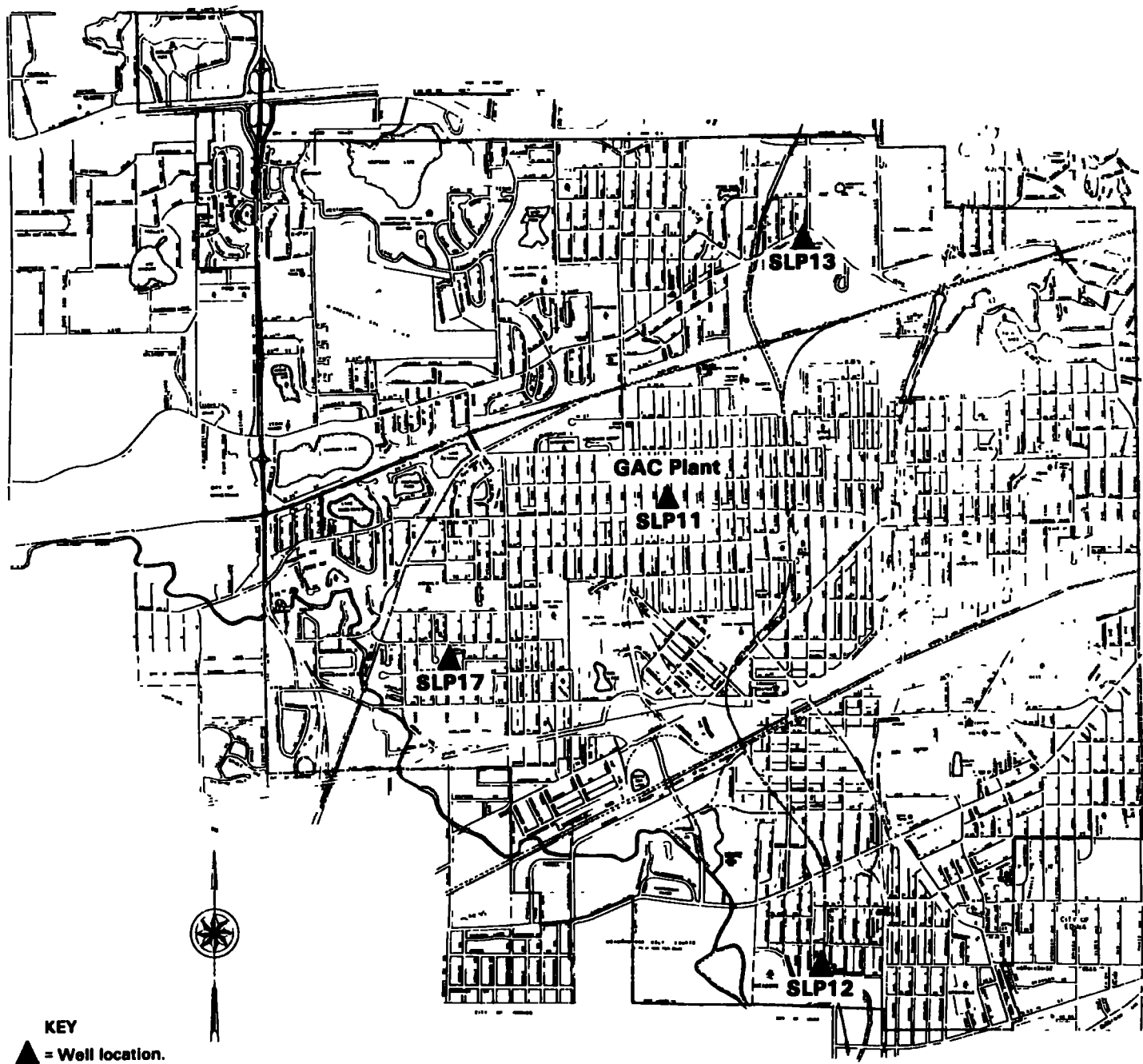


Figure 1 Location of Mt. Simon - Hinkley Monitoring Wells and St. Louis Park GAC Water-treatment Plant

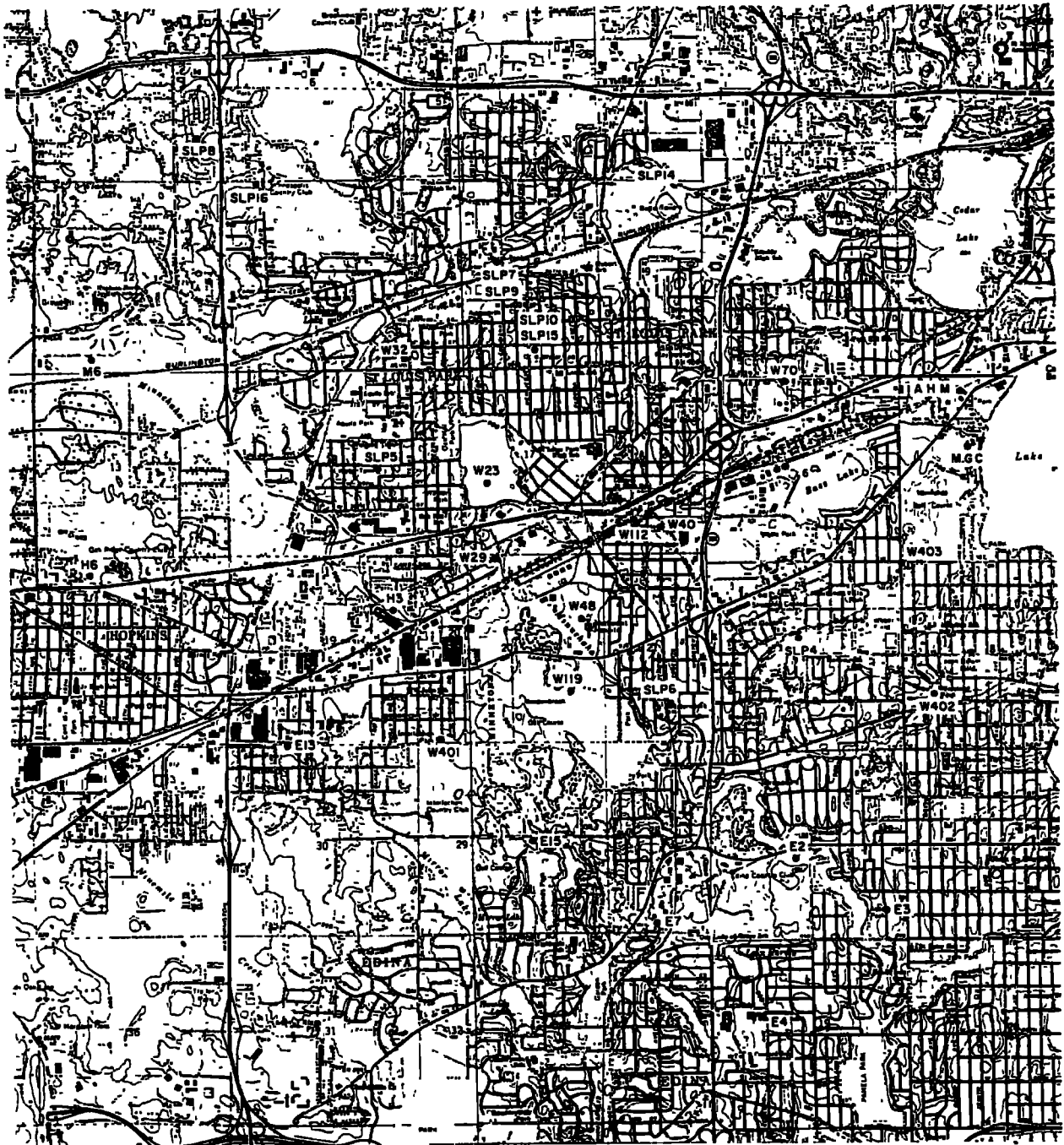


Figure 2 Location of Prairie du Chien-Jordan Aquifer Wells

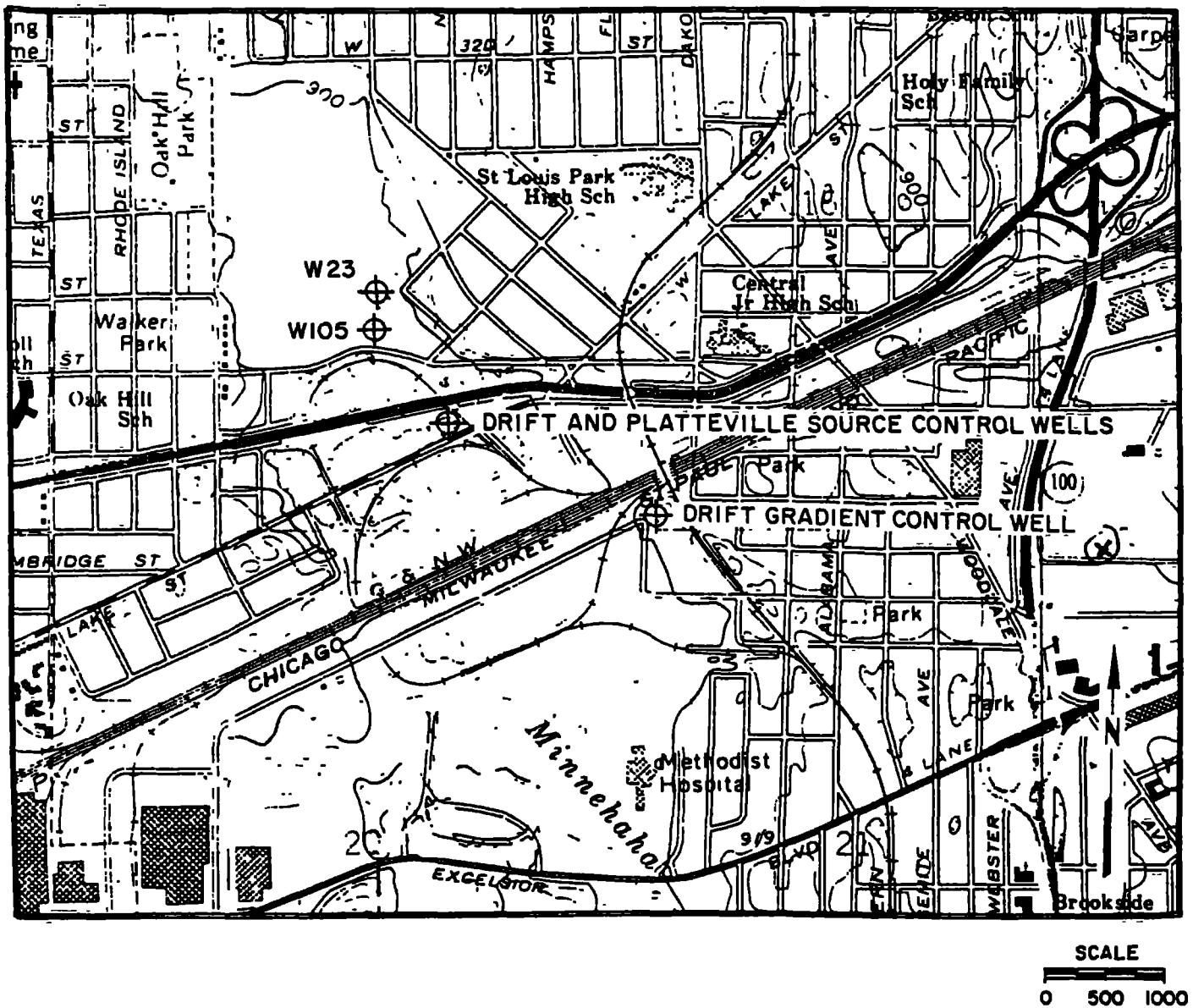
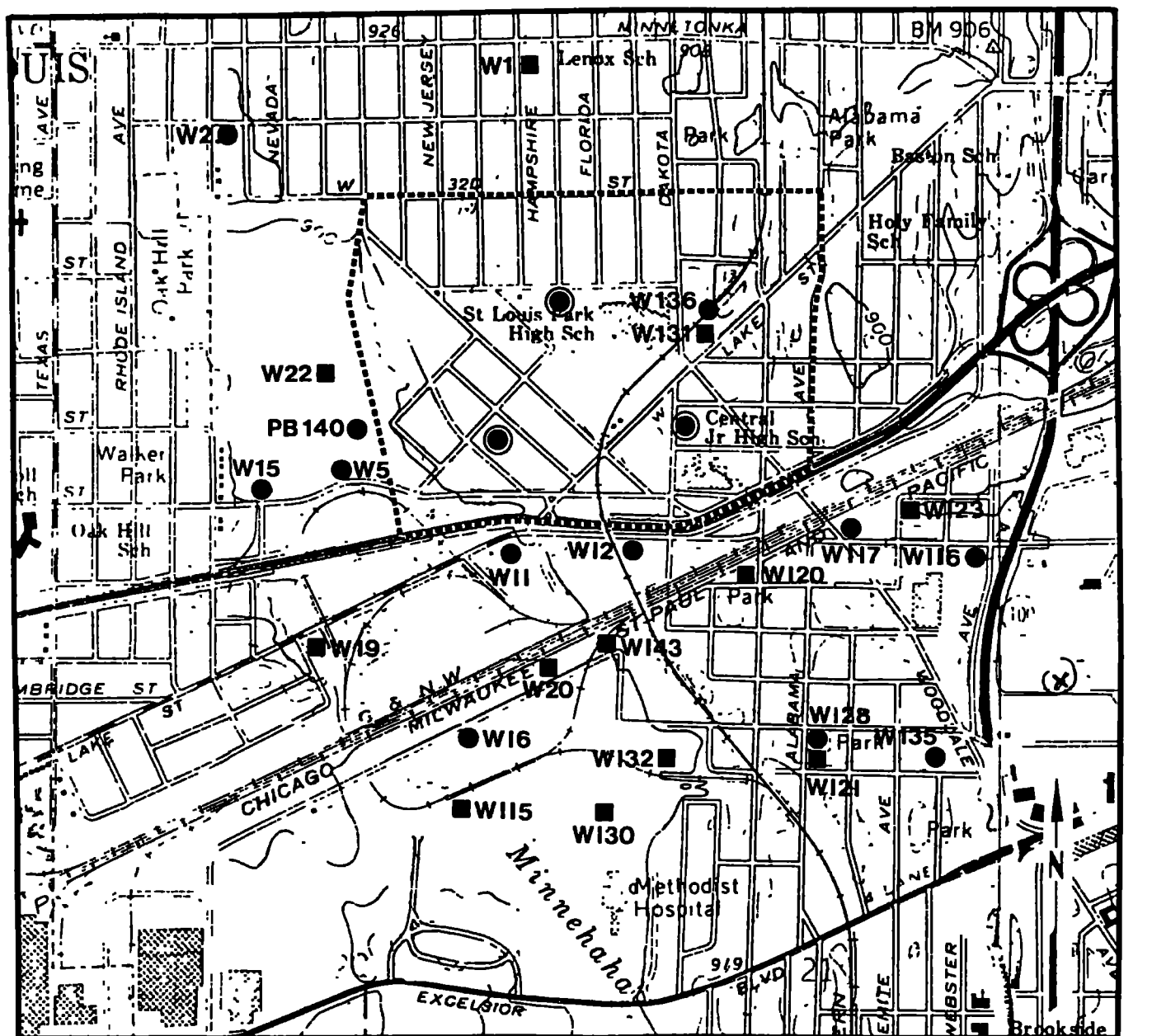


Figure 3 Location of Source and Gradient Control Wells



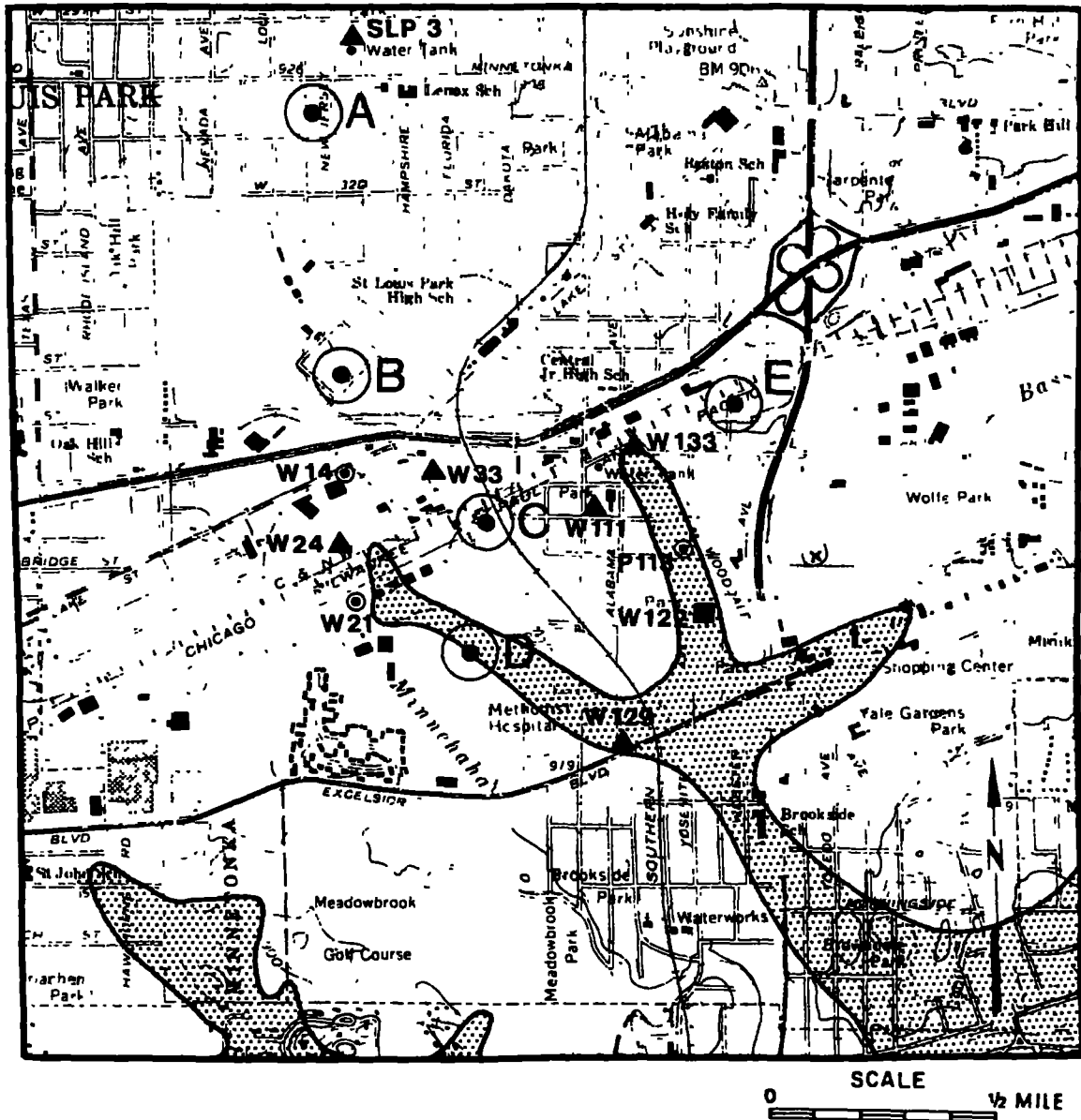
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EXPLANATION

- EXISTING DRIFT WELLS
- EXISTING PLATTEVILLE WELLS
- PROPOSED DRIFT AND PLATTEVILLE WELLS
- NORTHERN AREA REMEDIAL INVESTIGATION

Figure 4 Location of Drift-Platteville Monitoring Wells

Reference: MGS, Miscellaneous Map Series,
M-57, Plate 1 of 2, Bedrock Geology,
by Bruce A. Bloomgren, 1985



EXPLANATION

- ▲ W33 LOCATION AND PROJECT WELL NUMBER
- ▲ OBSERVATION WELL COMPLETED IN ST. PETER AQUIFER
- OBSERVATION WELL COMPLETED IN BASAL ST. PETER CONFINING BED
- PROPOSED ST. PETER MONITORING WELLS
- ◎ WELL IN WHICH WATER LEVELS WERE MONITORED WITH A DIGITAL RECORDER DURING PART OF 1978-81
- ▨ BEDROCK VALLEY/CONTACT WHERE UNCONSOLIDATED DRIFT DEPOSITS OVERLIE ST. PETER SANDSTONE

Figure 5 Proposed and Existing Well Locations and Bedrock Valley

Identification of Wells to be Monitored

The RAP specifies the majority of wells to be monitored, but leaves the identification of 30 Drift-Platteville Aquifer wells to this Plan. Specifically, Section 9.6 of the RAP requires 30 Drift-Platteville Aquifer monitoring wells to be sampled semi-annually during the first year, annually during the second and third years, thereafter, 20 wells are to be sampled biennially. Thirty candidate Drift-Platteville Aquifer monitoring wells have been chosen including W131, W136, the six new Drift-Platteville Aquifer wells installed for the Northern Area Remedial Investigation, eleven other existing Drift Aquifer monitoring wells, and eleven other Platteville Aquifer monitoring wells (Figure 4). The 22 other existing Drift-Platteville Aquifer monitoring wells selected for monitoring are as follows:

<u>Drift Aquifer Monitoring Wells</u>	<u>Platteville Aquifer Monitoring Wells</u>
W2, W5	W1, W19
W11, W12	W20, W22
W15, W16	W115, W120
W116, W117	W121, W123
W128, W135	W130, W132
PB140	W143

The objectives of monitoring ground-water in the Drift-Platteville Aquifer are to: 1) assess changes in the extent of contamination, and 2) to evaluate the effectiveness of the source and gradient control well systems and any other remedy implemented in the Drift-Platteville Aquifer. In order to address the first objective, Drift-Platteville Aquifer monitoring wells that provide adequate coverage of the area surrounding the contaminant source area were chosen. While only two upgradient or cross-gradient wells were chosen (W1 and W2) most of the selected wells are spread out around the area downgradient from the site and bog contaminant source areas (Figure 4).

The second objective is addressed by selecting wells that will provide both water level and water quality data that will help assess the effectiveness of the source and gradient control well systems. In this regard, the water quality data are judged to be more significant than the water level data, because the purpose of these systems is to control the distribution of contaminants. Therefore, wells outside of the hydraulic influence of a pumping well should reflect the influence of the pumping well on water quality in the aquifer. Also, the pumping wells themselves will be monitored quarterly in accordance with the RAP, and pumping test data will be used to determine the hydraulic influence of the pumping wells. Therefore, the wells shown on Figure 4 are selected primarily for the water quality samples they will provide.

GROUND-WATER SAMPLING PROCEDURES

An important distinction is made between the sampling procedures for active pumping wells (eg. municipal wells) and for non-pumping monitoring wells. Active pumping wells are used on a regular basis, have dedicated pumps and associated plumbing, and have sample taps for collecting samples. Non-pumping monitoring wells may be new, or may have not been pumped for several years, and most require pumping and associated equipment for sampling. Another distinction is that the active pumping monitoring wells are typically located inside buildings whereas monitoring wells are not.

With these considerations in mind, the Initial Sampling Plan has been developed so that the ground-water monitoring program in each aquifer meets the requirements and intent of the RAP. Ground-water monitoring will be conducted in accordance with the procedures given in the Quality Assurance Project Plan (QAPP), and with "Procedures for Ground-Water Monitoring: Minnesota Pollution Control Agency Guidelines", April 1985. Well logs for existing wells that will be monitored, which have not been presented in any other submittal, are given in Appendix A.

Water Level Measurements

Water level measurements will be made using electric tapes or weighted steel tapes. Steel tapes will be used whenever possible because of their generally greater precision compared to electric tapes. Water level measurements using steel tapes will be made by suspending a known length of tape in the well so that the bottom end of the tape is below the water level. The lower portion of tape will be coated with blue chalk that exhibits a noticeable color change when wetted. The water level measurement will be obtained by subtracting the length of wetted tape from the total length of tape suspended below the measuring point of each well.

If reliable water marks on chalked portions of steel tapes can not be discerned because of water on the inside of the well casing or pump discharge pipe, then an electric tape will be used for water level measurements. Using the electric tape, the probe at the end of the tape will be lowered slowly in the well until contact with the water is made. Because of surface tension, readings of the water level made when the probe enters the water will differ from readings made when the probe leaves the water, thus breaking surface tension. To standardize these measurements, the second reading will always be used (i.e., the reading made when the probe leaves the water).

Water level measurement made for the purpose of defining ground-water flow patterns in a particular aquifer will be performed independently from ground-water sampling, as a discrete event

(probably lasting one or two days). The wells will be revisited for sampling, and measurements to determine the volume of water in the well will be made at that time.

Sample Collection at Active Pumping Wells

At active pumping wells the sampling team will first determine that the wells have actually been pumping during the period preceding sampling. This information may be derived from inspecting flow recorders or from interviewing knowledgeable persons regarding the wells (water department employees, well owners, etc.). The information will be documented in the field notes of the sampling team.

Water level measurements will then be made, if practical. The normal operation of the well will not be interrupted for the purpose of measuring water levels. An electric tape will be used to measure water levels in pumping wells. Sampling will proceed by filling the required containers with water from the sampling tap as near to the well head as possible, and before any holding tanks or treatment is encountered. The only exception to this is the GAC plant monitoring under RAP section 4.3 which includes treated-water monitoring.

If it can not be determined that a well has been pumping at some time during the 24 hour period preceding sampling, or if it is known the well was not pumping, then the well shall be purged until field measurements of temperature, pH, and specific conductance have stabilized after at least three well volumes have been removed from the well. These measurements, water levels, and the amount of water pumped will be recorded in the field notes.

Sample Collection at Non-Pumping Monitoring Wells

The vast majority of the non-pumping monitoring wells are constructed with a 4-inch diameter well casing. One of the proposed Drift Aquifer monitoring wells is a two-inch piezometer and one of the proposed St. Peter Aquifer monitoring wells is a 1-1/4-inch diameter piezometer. The 4-inch and 2-inch diameter wells will be purged with stainless steel submersible pumps, while the piezometer will be purged with a peristaltic pump. The only materials that the water will come in contact with in the submersible pumps are stainless steel and Teflon. Also, there are no lubricated surfaces within the submersible pumps that would contaminate the samples. Tygon tubing will be used with the peristaltic pump, and as the discharge line for the submersible pumps.

The general procedure at monitoring wells will be to first measure the water level and, for the initial sampling round, the depth of the well. The amount of water in one well volume will then be calculated. The submersible pump will be lowered into the well and will be maintained in a position

near the top of the water column to ensure proper purging of the well. During purging, measurements of temperature, pH, and specific conductance will be made at intervals of one well volume until the values for these parameters, in three successive measurements, stabilize. Samples for chemical analysis will then be collected according to the procedures given in the QAPP. The QAPP also identifies the sample handling, quality control (field and trip blank schedule), and Chain of Custody procedures that will be followed during this program.

The discharge from purging monitoring wells will be handled in accordance to the Contingency Plan. In general, if a visible sheen can be seen on the water surface, the discharge will be routed to the sanitary sewer. Otherwise, the storm sewer or surface water discharge will be used.

Non-dedicated ground-water sampling or monitoring equipment that comes in contact with the ground water will be decontaminated between uses. The decontamination procedure includes the following steps:

- o scrub in soap and water,
- o rinse with deionized water,
- o rinse with acetone,
- o rinse with hexane,
- o rinse with acetone,
- o rinse with deionized water, and
- o air dry for 15 minutes.

Contingency Plan

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ANALYTICAL PROGRAM

Table 1 shows the ground-water monitoring summary as prescribed in the RAP. Indicated on the table are the analyses required. Expanded analyses including some priority and conventional pollutants may also be required according to RAP Section 9.3.3. Details of all analytical methodology can be found in the QAPP. Organic analyses and metals analyses will be performed at ERT's Concord, Massachusetts laboratory facility. The Concord laboratory is the primary laboratory and all PAH and phenolics analyses will be performed at that location. The inorganic analyses will be performed at ERT's Houston, Texas laboratory facility. The laboratories have agreed to provide a turnaround time of 28 working days from the receipt of samples to the submittal of analytical reports. The laboratory will notify the City of St. Louis Park if it can not meet this turnaround time.

Ground-water monitoring will include two methods of PAH analyses depending upon the anticipated PAH concentration levels. Low level (nanograms per liter or part per trillion) PAH analyses will be performed utilizing selected ion monitoring gas chromatography mass spectrometry. This method will be used to analyze samples from drinking water wells and from other wells for which the RAP requires drinking water criteria to be enforced (e.g., St. Peter Aquifer monitoring wells). Non-criteria level (micrograms per liter or part per billion) PAH analyses, using EPA Method 625, will be performed on samples from wells that have historically contained elevated PAH concentrations (e.g., part per million levels in wells W23 and W105), and initially on wells that are not subject to the RAP's requirements for meeting drinking water criteria (e.g., Drift-Platteville Aquifer monitoring wells).

Two methods are required for PAH analyses because the low level part per trillion method is not appropriate for samples containing in excess of approximately 20 micrograms per liter of total PAH. Analysis of samples containing total PAH concentrations over 20 micrograms per liter, if performed with the low level method, requires multiple dilutions and increases the risk of cross-contamination of the samples. This decreases the reliability of the data. Not only will multiple dilutions increase the variability of measurements, but critical quality control information (e.g., surrogate recoveries) is lost. Therefore, for samples containing greater than 20 micrograms per liter of total PAH the analytical method that will be used is EPA Method 625 as described in the Quality Assurance Project Plan (Section 4.6).

The EPA Method 625 analysis will be performed on one-liter samples, and will have detection limits of 10 micrograms per liter. For wells that are tested with this non-criteria method, if the analytical results of the first sampling indicates total PAH concentrations less than 20 micrograms per liter, the low level method will be used to analyze samples from subsequent sampling rounds. This

procedure will allow an evaluation of long-term PAH concentrations around the fringe of PAH contamination in the Drift-Platteville Aquifer.

Depending on the circumstances and the actual PAH level, first-round analytical results using the low level method that exceed 20,000 nanograms per liter of total PAH will indicate a switch to EPA Method 625 for subsequent sampling rounds.

REPORTING

The analytical reporting requirements of the Consent Decree and RAP are identified in Part K of the Consent Decree, and Sections 3.4, 4.3.5, 12.1.1, and 12.1.2 of the RAP. Part K requires Reilly to submit quarterly progress reports on October 10, 1986, January 10, 1987, April 10, 1987, and July 10, 1987. These progress reports will contain analytical reports as specified in Section 5.0 of the QAPP for this Initial Sampling Plan. The analytical results for samples collected in accordance with this Initial Sampling Plan, but after the reporting period for the July 10, 1987 progress report, will be provided in next regularly scheduled annual progress report on March 15, 1988.

RAP Section 3.4 requires the City to submit an annual report that presents the results of all monitoring during the previous calendar year. The reports are due each March 15, beginning in 1987. The monitoring results that will be presented in the annual reports will include all water level measurements and chemical analyses that have not been presented in previous reports (e.g., the St. Peter Remedial Investigation Report will present all of the data for the St. Peter Aquifer). Interpretive maps and tables will be included in the annual reports, as specified in RAP Section 3.4(B) and (C). Also the effectiveness of the source and gradient control well systems in the Drift-Platteville Aquifer will be discussed in the annual report.

The reporting requirement for each aquifer, and for the GAC treatment plant, are described below.

GAC Treatment Plant

RAP Section 4.3.5 requires the City to submit an annual report that presents the results of all monitoring of the GAC treatment system. Analytical results for wellhead water, feed water, and treated water will be included in this report. The report will also describe briefly the operating performance of the GAC plant during the previous calendar year. The GAC plant annual reports are due each March 15th, beginning in 1987.

Mt. Simon-Hinckley Aquifer

The monitoring data for the Mt. Simon-Hinckley Aquifer will be included in the annual report due March 15, 1988. In addition to the results of all water level measurements and chemical analyses, the report will contain a map showing each well sampled with the concentrations of Other PAH, Carcinogenic PAH, and the sum of benzo(a)pyrene and dibenz(a,h)anthracene labelled by the location of each well in accordance with RAP Section 3.4(C). Since the Mt. Simon-Hinckley Aquifer wells are monitored on an annual basis, there will be only one sampling event to report.

Ironton-Galesville Aquifer

The monitoring data for the Ironton-Galesville Aquifer will be included in the annual report due March 15, 1988. Since well W105 is the only well that will be sampled in this aquifer and only one other well (W38) will be used for water level measurements, the monitoring data will be reported in tabular form as well as in map form as required by RAP Section 3.4.

Prairie du Chien-Jordan Aquifer

The monitoring data for the Prairie du Chien-Jordan Aquifer will be included in the annual report due March 15, 1988. The results of all water level measurements and chemical analyses will be included. For each of the quarterly measuring periods a water level contour map will be prepared with elevations labelled at each well. For each sampling event, a map showing each well sampled with the concentrations of Other PAH, Carcinogenic PAH, and the sum of benzo(a)pyrene and dibenz(a,h)anthracene labelled by the location of each well will be prepared in accordance with RAP Section 3.4(C).

St. Peter Aquifer

The monitoring data for the St. Peter Aquifer will be reported in the St. Peter Remedial Investigation Report, in accordance with RAP Section 8.1.4. The results of all water level measurements and chemical analyses will be included. For each measuring period in the St. Peter Aquifer, a water level contour map will be prepared with elevations labelled at each well. For each sampling event, a map showing each well sampled with the concentrations of Other PAH, Carcinogenic PAH, and the sum of benzo(a)pyrene and dibenz(a,h)anthracene labelled by the location of each well will be prepared in accordance with RAP Section 3.4(C). In the event that the St. Peter Remedial Investigation Report is delayed beyond March 15, 1988, the monitoring data for the St. Peter Aquifer will be included in the annual report due March 15, 1988.

Drift-Platteville Aquifer

The monitoring data for the Drift-Platteville Aquifer will be included in the annual report due March 15, 1988, and in the Northern Area Remedial Investigation Report. The results of all water level measurements and chemical analyses will be included in both reports. For each measuring period in the Drift-Platteville Aquifer a water level contour map will be prepared with elevations labelled at each well. For each sampling event, a map showing each well sampled with the concentrations of Other PAH, Carcinogenic PAH, and the sum of benzo(a)pyrene and dibenz(a,h)anthracene labelled by the location of each well, and a map with phenolics concentrations labelled by the location of each well

will be prepared in accordance with RAP Section 3.4. The Drift-Platteville Aquifer monitoring data will be included in the Northern Area Remedial Investigation Report because of its relevance to providing a further definition of the nature and extent of contamination in the Northern Area. The same data will be included in the annual report to support a discussion of the results with respect to the effectiveness of the source and gradient control well systems.

RAP Sections 12.1.1 and 12.1.2 describe the re-sampling and analysis requirements in the event that samples from active municipal drinking water wells yield analytical results above advisory levels or drinking water criteria. Upon receipt of written analytical reports from the laboratory, the City will immediately notify the Regional Administrator, the Director, and the Commissioner of the exceedance. The notification will include the analytical data report as provided by the laboratory. The contents of these reports are discussed in detail in Section 10 of the QAPP for this Initial Sampling Plan.

APPENDIX A

WELL LOGS

U.S. GEOLOGICAL SURVEY
WATER RESOURCES DIVISION
702 POST OFFICE BUILDING
ST. PAUL, MINNESOTA 55101

PROVISIONAL RECORDS
Subject to Revision

Table 1. Data on municipal wells in the St. Louis Park area, Minnesota—Continued

Township and range	Site identification (latitude and longitude)	Minnesota unique well number	Project well number	Owner name or other identifier	Driller	Date drilled	Driller's log	Land surface altitude, in feet	Reported depth of well, in feet	Casing diameter, in	Aperture(s) open to well bore	Water level, in feet	Date measured	Field measurement status	Remarks
117N21W60E1	445615093212301	206403	W 112	Old St. Louis Park well #1	McCarthy	05-32	0-109 Gd 139-278 Gd 218-398 Gd 318-486 Gd	917.5	540	16 in. 0-312 12 in. 194-274	In 1932 Opt-GJ In 1978 Opt	83	2-4-82	0, M	Also included in table
117N21W60E1	445701093215801	206401	SLP 1	St. Louis Park municipal well 1	Max Ranner	00-38	0-104 Gd 134-136 Gd 136-236 Gd 236-300 Gd	925	250	16 in. 0-104	Opt-Gd	60	0-0-59	A	
117N21W60E2	445659093220201	206462	SLP 2	St. Louis Park municipal well 2	do	00-38	0-104 Gd 134-136 Gd 136-236 Gd 236-300 Gd	925	250	16 in. 0-104	Opt-Gd	60	0-0-59	A	
117N21W60E3	445701093215803	206440	W 113	St. Louis Park municipal well 3	McCarthy	08-39	0-103 Gd 133-118 Gd 118-230 Gd 230-286 Gd	922	286	28 in. 0-103	Opt-Gd	49	2-4-82	P	Latitude is 445702 Also included in table
02N24W07E04	445546093202201	206542	SLP 4	St. Louis Park municipal well 4	Layne- Minnesota	09-46	0-89 Gd 89-119 Gd 119-250 Gd 250-300 Gd 300-411 Gd 411-483 Gd 483-503 Gd	900	503	28 in. 0-40 18 in. 0-304	Opt-GJ Gd	85	9-27-86 PROVISIONAL RECORD Subject to Revision	P	
117N21W60E1	445611093220301	203196	SLP 5	St. Louis Park municipal well 5	do	10-47	0-109 Gd 139-120 Gd 130-132 Gd 132-230 Gd 230-286 Gd 286-407 Gd 407-465 Gd	930	465	28 in. 0-115 20 in. 0-305	Opt-GJ	109	2-4-82	P	
117N21W60E1	445520093211401	206457	SLP 6	St. Louis Park municipal well 6	do	03-48	0-90 Gd 90-122 Gd 122-127 Gd 127-190 Gd 230-417 Gd 417-480 Gd	915	480	28 in. 0-107 20 in. 0-303	Opt-GJ	102	2-4-82	P	
117N21W60E1	445702793221701	206436	SLP 7	St. Louis Park municipal well 7	do	05-52	0-75 Gd 75-97 Gd 97-100 Gd 100-210 Gd 210-360 Gd 360-400 Gd 400-486 Gd	905	446	28 in. 0-80 20 in. 0-247	Opt-GJ	87	2-4-82	P	Latitude is 445730
117N22W01E1	445607093241001	227964	SLP 8	St. Louis Park municipal well 8	Bergeson- Cawell	00-55	0-108 Gd 138-126 Gd 126-132 Gd 132-242 Gd 242-303 Gd 303-413 Gd 413-495 Gd 495-507 Gd	940	507	28 in. 0-253 16 in. 0-343	GJ-Gd	130	2-4-82	P	Longitude is 0932408
117N21W60E2	445730093222201	206437	SLP 9	St. Louis Park municipal well 9	Layne- Minnesota	06-56	0-69 Gd 69-120 Gd 120-220 Gd 220-275 Gd 275-300 Gd 300-473 Gd	905	473	28 in. 0-81 16 in. 0-289	Opt-GJ	70	6-6-56	P	
117N21W60E2	445700093221304	206442	SLP 10	St. Louis Park municipal well 10	Keya	09-55	0-105 Gd 105-125 Gd 125-200 Gd 200-409 Gd 409-500 Gd	936	500	28 in. 0-106 16 in. 0-315	Opt-GJ	111	2-4-82	P	Latitude is 445702 Longitude is 0932404

PROVISIONAL RECORDS
Subject to Revision

PROVISIONAL RECORDS
Subject to Revision

U.S. GEOLOGICAL SURVEY
WATER RESOURCES DIVISION
702 POST OFFICE BUILDING
ST. PAUL, MINNESOTA 55101

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PROVISIONAL RECORDS
Subject to Revision

Subject to Revision

Table __—Data on municipal wells in the St. Louis Park area, Minnesota—Continued

Township and range	Site Identification (Latitude and Longitude)	Minnesota unique well number	UNCS project well number	Owner name or other identifiers	Driller	Date drilled	Driller's log	Land surface altitude, in feet	Reported depth of well in feet	Casing diameter of well in feet	Aquifer(s) open to well bore	Water level, in feet	Date measured	Field measurement status	Remarks
117N21W080005	4457009320201	206139	SLP 11	St. Louis Park municipal well 11	Bergersen-Caswell	11-60	0-101 Q d 101-120 O pl 120-200 O sp 200-408 O ps 408-505 C j 505-530 C al 530-683 C f 683-745 C lg 745-853 C eo 853-955 C ne 955-1093 C h	920	1093	24 in. 0-101 16 in. 10-880	Qns-Ch	258	2-4-82	P	Latitude is 445704 Longitude is 0932104
117N21W080002	445526093211402	206456	SLP 12	St. Louis Park municipal well 12	Kaye	10-65	0-96 Q d 96-127 O pl 127-132 O gl 132-232 C sp 232-447 C po 447-505 C j 505-530 C al 530-683 C f 683-745 C lg 745-853 C eo 853-955 C ne 955-1093 C h	915	1095	30 in. 0-99 24 in. 0-270 16 in. 0-900	Qns-Ch	245	10-65	P	Latitude is 445523 Longitude is 0932112
117N21W080001	445754093212201	206124	SLP 13	St. Louis Park municipal well 13	Layne-Minnesota	07-64	0-94 Q d 94-101 O pl 101-212 C sp 212-270 C po 270-386 C j 386-460 C f 460-490 C lg 490-655 C eo 655-714 C ne 714-770 C h 770-917 C i 917-1040 C j 1040-1045 C k	900	1040	30 in. 0-95 24 in. 0-212 16 in. 0-891	Qns-Pch	255	07-64	P	Longitude is 0932123
PROVISIONAL RECORDS Subject to Revision															
117N21W080002	445513093213602	227965	SLP 14	St. Louis Park municipal well 14	Bergersen-Caswell	09-65	0-94 Q d 94-98 O pl 98-265 C sp 265-375 C po 375-475 C j 475-485 C lg	900	485	30 in. 0-94 24 in. 0-253 16 in. 0-309	Cj	89	2-4-82	P	Latitude is 445754 Longitude is 0932123
117N21W080006	4457009320202	215447	SLP 15	St. Louis Park municipal well 15	Bergersen-Caswell	00-69	0-102 Q d 102-124 O pl 124-200 C sp 200-408 C po 408-482 C j 482-503 C lg	925	503	30 in. 0-102 24 in. 0-425	Cj	110	2-4-82	P	Latitude is 445704
117N21W070004	445750093234801	203187	SLP 16	St. Louis Park municipal well 16	TVI-Statco	07-73	0-105 Q d 105-124 O pl 124-258 C sp 258-298 C po 298-310 C j 310-495 C lg 495-500 C k	920	500	50 in. 0-310 24 in. 0-425	Cj	120	2-4-82	P	Presently under construction
117N21W080003	445631093230303	—	SLP 17	St. Louis Park municipal well 17	Layne-Minnesota	00-20	0-95 Q d 95-120 O pl 120-210 C sp 210-270 C po 270-390 C j 390-470 C lg 470-780 C k	925	780	16 in. 0-95 12 in. 0-286	Qns-Cj Cjg	—	—	P	Presently under construction
117N22W080004	445514093241301	204573	HDP 1	Hopkins municipal well 1	McCarthy	00-20	0-95 Q d 95-120 O pl 120-210 C sp 210-270 C po 270-390 C j 390-470 C lg 470-780 C k	925	780	16 in. 0-95 12 in. 0-286	Qns-Cj Cjg	—	—	P	Presently under construction
PROVISIONAL RECORDS Subject to Revision															
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U.S. GEOLOGICAL SURVEY
WATER RESOURCES DIVISION
702 POST OFFICE BUILDING
ST. PAUL, MINNESOTA 55101

PROVISIONAL RECORDS
Minnesota Statewide

Table 1.—Data on municipal wells in the St. Louis Park area, Minnesota—Continued

Township and range	Site identification (latitude and longitude)	Unique well number	Project well number	Owner name or other identifier	Driller	Date drilled	Well depth, in feet	Land surface altitude, in feet	Reported depth of well, in feet	Casing diameter and depth, in feet	Aquifer(s) open to well bore	Water level, in feet, subject to revision	Date measured	Field measurement status	Remarks
117N22E24N2C	44550709324001	207995	EDP 2	Hopkins municipal well 2	McCarthy	00-38	0-87 (N) 17-117 (N) 117-220 (N) 220-290 (N) 290-405 (N) 405-475 (N) 475-540 (N) 540-610 (N) 610-720 (N) 720-728 (N)	920	728	16 in. 0-89 12 in. 0-202	Op-CJ	72	1948	AK	
117N22E19N1C	44550709324001	208108	EDP 3	Hopkins municipal well 3	do	00-48	0-80 (N) 10-110 (N) 110-116 (N) 116-225 (N) 225-240 (N) 240-260 (N) 260-275 (N) 275-280 (N) 280-290 (N) 290-300 (N)	920	475	24 in. 0-86 20 in. 0-292 16 in. 0-132	Op-CJ	43	3-3-82	P	
117N22E13C	44550709325001	204068	EDP 4	Hopkins municipal well 4	Bergeson-Cornwall	05-54	0-144 (N) 144-171 (N) 171-175 (N) 175-335 (N) 335-350 (N) 350-530 (N) 530-548 (N)	900	548	—	—	164	3-3-82	P	
117N22E24N2C	44550709324001	204570	EDP 5	Hopkins municipal well 5	do	05-67	0-179 (N) 179-260 (N) 260-317 (N) 317-427 (N) 427-489 (N) 489-500 (N)	967	500	30 in. 0-280 24 in. 217-320 16 in. 0-382	Op-CJ	141	3-3-82	P	
117N22E24N2C	44550709324001	112228	EDP 6	Hopkins municipal well 6	do	09-77	0-134 (N) 134-165 (N) 165-281 (N) 281-313 (N) 313-325 (N) 325-345 (N) 345-400 (N)	995	595	30 in. 0-132 24 in. 0-354	Op-CJ	150	3-3-82	P	
117N22E24N2C	44550709324001	208011	MDK 1	Minnetonka municipal well 1	do	08-55	0-229 (N) 229-269 (N) 269-307 (N) 307-513 (N)	1045	513	—	—	—	—	AR	
117N22E24N2C	44550709324001	20810	MDK 2	Minnetonka municipal well 2	Tr-I-State	03-62	0-251 (N) 251-270 (N) 270-384 (N) 384-427 (N) 427-530 (N) 530-619 (N)	—	619	16 in. 0-295 10 in. 0-545	CJ	220	3-62	P	
117N22E24N2C	44550709324001	204470	MDK 3	Minnetonka municipal well 3	Tr-I-State	10-63	0-118 (N) 118-247 (N) 247-378 (N) 378-461 (N) 461-465 (N)	921	465	24 in. 0-123 20 in. 0-196 18 in. 0-393	CJ	39	10-63	P	
117N22E24N2C	44550709324001	171021	MDK 3A	Minnetonka municipal well 3A	E. H. Renner	03-81	0-105 (N) 105-120 (N) 120-195 (N) 195-220 (N) 220-382 (N) 382-465 (N) 465-468 (N)	—	468	30 in. 0-129 24 in. 0-186 16 in. 0-254	Op-CJ	53	01-81	P	
117N22E24N2C	44550709324001	205082	MDK 4	Minnetonka municipal well 4	Bergeson-Cornwall	09-57	0-172 (N) 172-315 (N) 315-338 (N) 338-530 (N)	960	530	—	—	100	9-16-57	—	
117N22E24N2C	44550709324001	205133	MDK 5	Minnetonka municipal well 5	do	12-56	0-253 (N) 253-279 (N) 279-338 (N) 338-460 (N) 460-545 (N) 545-561 (N)	1000	561	—	—	131	12-12-56	—	

U.S. GEOLOGICAL SURVEY
WATER RESOURCES DIVISION
702 POST OFFICE BUILDING
ST. PAUL, MINNESOTA 55101

PROVISIONAL RECORDS
Minnesota Statewide

117N22E24N2C	44550709324001	208011	MDK 1	Minnetonka municipal well 1	do	08-55	0-229 (N) 229-269 (N) 269-307 (N) 307-513 (N)	1045	513	—	—	—	—	AR	
117N22E24N2C	44550709324001	20810	MDK 2	Minnetonka municipal well 2	Tr-I-State	03-62	0-251 (N) 251-270 (N) 270-384 (N) 384-427 (N) 427-530 (N) 530-619 (N)	—	619	16 in. 0-295 10 in. 0-545	CJ	220	3-62	P	
117N22E24N2C	44550709324001	204470	MDK 3	Minnetonka municipal well 3	Tr-I-State	10-63	0-118 (N) 118-247 (N) 247-378 (N) 378-461 (N) 461-465 (N)	921	465	24 in. 0-123 20 in. 0-196 18 in. 0-393	CJ	39	10-63	P	
117N22E24N2C	44550709324001	171021	MDK 3A	Minnetonka municipal well 3A	E. H. Renner	03-81	0-105 (N) 105-120 (N) 120-195 (N) 195-220 (N) 220-382 (N) 382-465 (N) 465-468 (N)	—	468	30 in. 0-129 24 in. 0-186 16 in. 0-254	Op-CJ	53	01-81	P	
117N22E24N2C	44550709324001	205082	MDK 4	Minnetonka municipal well 4	Bergeson-Cornwall	09-57	0-172 (N) 172-315 (N) 315-338 (N) 338-530 (N)	960	530	—	—	100	9-16-57	—	
117N22E24N2C	44550709324001	205133	MDK 5	Minnetonka municipal well 5	do	12-56	0-253 (N) 253-279 (N) 279-338 (N) 338-460 (N) 460-545 (N) 545-561 (N)	1000	561	—	—	131	12-12-56	—	

PROVISIONAL RECORDS
Subject to Revision

411857

PROVISIONAL RECORDS
Subject to Revision

411856

PROVISIONAL RECORDS
Subject to Revision

Table 1—Data on municipal wells in St. Louis Park area, Minnesota—Continued

PROVISIONAL RECORDS
Subject to Revision

Well number	Site identification (latitude and longitude)	Minnesota project well number	Owner name or other identifier	Driller	Date drilled	Driller's log	Land surface altitude, in feet	Reported depth of well, in feet	Casing diameter, in	Aquifer(s) open to well bore	Water level, in feet	Date measured	Field measurement status	Remarks
117N224120C1	44570309324501	204024	Minnetonka municipal well 6	Kays	05-67	0-101 : M 101-117 : M 117-133 : M 133-248 : M 248-310 : M 310-392 : M 392-486 : M 486-488 : M	—	488	24 in. 0-103 : M 20 in. 0-320 : M 16 in. 312-394	CJ	—	—	—	
117N224120C2	44570309324502	208012	Minnetonka municipal well 7	do	07-67	0-104 : M 104-112 : M 112-121 : M 121-135 : M 135-249 : M 249-304 : M 304-392 : M 392-486 : M 486-488 : M	—	486	24 in. 0-114 : M 20 in. 0-315 : M 16 in. 309-381 : M 12 in. 284-397	CJ	—	—	—	
117N224220A4	445538093260101	208013	Minnetonka municipal well 8	—	08-58	0-155 : M 155-188 : M 188-339 : M 339-371 : M 371-559 : M 559-584 : M	—	584	8 in. 0-170 : M 6 in. 160-376	Op-CJ	116	00-00	AR	
117N224108B	445717093272701	204008	Minnetonka municipal well 9	E. H. Pernar	08-68	0-128 : M 128-160 : M 160-190 : M 190-250 : M 250-305 : M 305-305 : M	960	305	10 in. 0-312	Op-CJ	100	8-68	AR	U.S. GEOLOGICAL SURVEY WATER RESOURCES DIVISION 702 POST OFFICE BUILDING ST. PAUL, MINNESOTA 55101
117N224160U1	44563093274501	204140	Minnetonka municipal well 10	Layne- Minnesota	10-69	0-91 : M 91-126 : M 126-128 : M 128-230 : M 230-292 : M 292-420 : M 420-5-5 : M	940	505	24 in. 0-112 : M 20 in. 0-295 : M 16 in. 0-305	Op-CJ	85	10-8-69	P	U.S. GEOLOGICAL SURVEY WATER RESOURCES DIVISION 702 POST OFFICE BUILDING ST. PAUL, MINNESOTA 55101
117N224160U2	445635093274501	150356	Minnetonka municipal well 10A	do	03-81	0-90 : M 90-100 : M 100-124 : M 124-132 : M 132-223 : M 223-287 : M 287-405 : M 405-481 : M 481-486 : M	925	406	30 in. 0-106 : M 24 in. 0-254 : M 16 in. 0-302	Op-CJ	85	2-25-81	—	PROVISIONAL RECORDS Subject to Revision
117N224270C3	445485093274201	208014	Minnetonka municipal well 11	Bergerson- Caswell	08-70	0-181 : M 181-210 : M 210-272 : M 272-401 : M 401-495 : M 495-498 : M	—	498	24 in. 0-184 : M 16 in. 0-382	Op-CJ	83	00-707	—	
117N224030B	445608093265001	203717	Minnetonka municipal well 12	E. H. Pernar	06-71	0-130 : M 130-163 : M 163-198 : M 198-245 : M 245-332 : M 332-335 : M	—	535	24 in. 0-16 : M 16 in. 0-332	Op-CJ	115	6-71	P	
117N224520B1	445353093265001	205165	Minnetonka municipal well 13	Layne- Minnesota	04-72	0-224 : M 224-273 : M 273-398 : M 398-475 : M	—	475	24 in. 0-239 : M 16 in. 0-292	Op-CJ	—	—	P	PROVISIONAL RECORDS Subject to Revision
117N224520B2	445353093265002	132263	Minnetonka municipal well 13A	Hydro Engineering	06-78	0-193 : M 193-259 : M 259-336 : M 336-464 : M	—	464	24 in. 0-230 : M 16 in. 0-274	Op-CJ	98	00-00	P	

Table 1.—Data on municipal wells in't w. St. Louis Park area, Minnesota—Continued

Township and range	Site identification (latitude and longitude)	Minnesota well number	USGS project number	Owner name or other identifier	Driller	Date drilled	Driller's log	Land surface altitude, in feet	Reported depth of well, in feet	Casing diameter, in feet	Quifer(s) open to well bore	Water level, in feet	Date measured	Field measurement status	Remarks
117N24E28R01	44553109325201	204537	MRK 14	Minnetonka municipal well 14	E. H. Renner	05-72	0-172 172-195 195-204 204-305 305-360 360-400 400-555 CJ	—	555	24 in. 16 in. 0-367	Opn-CJ	175	00-00	P	
PROVISIONAL RECORDS Subject to Revision															
117N24E28R02	445530093255101	160021	MRK 14A	Minnetonka municipal well 14A	do	05-78	0-194 194-212 212-219 219-300 300-500 500-570 570-575 CJ	—	575	24 in. 0-196 20 in. 0-343 16 in. 0-395	Opn-CJ	195	11-22-78	P	
117N24E28R03	445530093255101	208016	MRK 15	Minnetonka municipal well 15	do	02-74	0-183 183-225 225-365 365-450 CJ	885	450	24 in. 0-192 16 in. 0-235	Opn-CJ	35	00-00	P	
117N24E28R04	445432093300201	150351	MRK 15A	Minnetonka municipal well 15A	Layne- Minnesota	04-78	0-185 185-227 227-350 350-444 CJ	—	444	24 in. 0-188 16 in. 0-238	Opn-CJ	27	4-12-78	P	
028N24W18R42	445442093202602	205591	EDN 1	Edina municipal well 1	—	1934	0-61 61-40 40-95 95-258 258-385 385-450 450-460 CJ	—	460	16 in. 0-61 12 in. 61-258	Opn-CJ	—	—	AR	
028N24W18R41	445442093202601	208399	EDN 2	Edina municipal well 2	—	1938	0-62 62-37 37-97 97-262 262-385 385-391 CJ	—	391	24 in. 0-62 0-62 16 in. 0-100	Opn-Opn	—	—	P	U.S. GEOLOGICAL SURVEY WATER RESOURCES DIVISION 702 POST OFFICE BUILDING ST. PAUL, MINNESOTA 55101
028N24W18R03	445430093195401	—	EDN 3	Edina municipal well 3	—	1949	—	—	422	—	—	76	2-3-82	P	
028N24W18R02	445405093203501	205561	EDN 4	Edina municipal well 4	Bergeson- Cassell	1950	0-40 40-110 110-270 270-410 410-500 CJ	900	500	24 in. 0-40 16 in. 0-270	Opn-CJ	80	—	P	
028N24W20R03	445266093194101	206377	EDN 5	Edina municipal well 5	Keys	1954	0-200 200-237 237-365 365-443 CJ	873	443	24 in. 0-136 20 in. 0-200 16 in. 0-257	Opn-CJ	75	—	P	PROVISIONAL RECORDS Subject to Revision
028N24W19R03	445348093204801	209564	EDN 6	Edina municipal well 6	do	06-54	0-48 48-110 110-118 118-278 278-408 408-493 493-503 CJ	900	505	24 in. 0-48 16 in. 0-316	Opn-CJ	90	—	P	
117N24E28R03	445420093211801	206478	EDN 7	Edina municipal well 7	do	03-55	0-132 132-159 159-162 162-290 290-324 324-453 453-545 545-547 CJ	950	547	24 in. 0-140 16 in. 0-350	Opn-CJ	112	—	P	
116N24W14R03	4453093213701	204884	EDN 8	Edina municipal well 8	Bergeson- Cassell	1953	0-220 220-364 364-445 445-472 CJ	870	472	24 in. 0-219 16 in. 0-232	Opn-CJ	49	—	P	
PROVISIONAL RECORDS Subject to Revision															

U.S. GEOLOGICAL SURVEY
WATER RESOURCES DIVISION
702 POST OFFICE BUILDING
ST. PAUL, MINNESOTA 55101

U.S. GEOLOGICAL SURVEY
WATER RESOURCES DIVISION
702 POST OFFICE BUILDING
ST. PAUL, MINNESOTA 55101

—Data on municipal wells in the St. Louis Park area, Minnesota—Continued

PROVISIONAL RECORDS
Subject to Revision

PROVISIONAL RECORDS
Subject to Revision

Well number	Site identification (latitude and longitude)	Minnesota unique well number	Owner name or other identifier	Driller	Date drilled	Driller's log	Land surface altitude, in feet	Reported depth of well, in feet	Casing diameter and depth, in feet	Aquifer(s) open to well bore	Water level, in feet	Remarks
11742143200	445347002213901	205588	Edina municipal well 9	Keys	10-57	0-121 04 122-131 04 131-135 04 135-139 04 279-433 04 433-515 04 515-525 04 525-100 04 700-780 04 780-865 04 865-999 04 999-1125 04 1125-1135 04	880	1130	24 in. 0-129 16 in. 0-563 10 in. 533-1010	pch	215	10-57
02812401001	445153023202101	206184	Edina municipal well 10	Bergerson-Cannell	10-63	0-183 04 183-305 04 305-403 04 403-466 04 466-522 04 522-664 04 664-729 04 729-876 04 876-999 04 999-1001 04	833	1001	24 in. 0-183 20 in. 0-651 16 in. 623-881	pch	143	10-63
02812401002	445153023202102	206183	Edina municipal well 11	do	04-63	0-179 04 179-304 04 304-402 04 402-402 04	833	1064	24 in. 0-182 16 in. 0-321	pch	—	—
11742143002	44531203230002	203614	Edina municipal well 12	Keys	05-64	0-111 04 111-128 04 128-277 04 277-411 04 411-479 04 479-542 04 542-713 04 713-813 04 813-918 04 918-108 04 108-108 04	980	1081	24 in. 0-116 16 in. 0-958	Do-pch	252	05-64
11742143001	44531203230001	203613	Edina municipal well 13	do	05-64	0-106 04 106-125 04 125-204 04 204-314 04 314-405 04 405-405 04	980	1496	24 in. 0-109 16 in. 0-129	CJ	97	05-64
11642140700	445159093225201	200913	Edina municipal well 14	Mueller Bros.	02-64	0-182 04 182-315 04 315-414 04 414-420 04	850	420	24 in. 0-182 16 in. 0-325	CJ	371	06-64
11742143008	445447093221001	207674	Edina municipal well 15	Layne-Munroe	11-67	0-91 04 91-111 04 111-205 04 205-365 04 365-400 04 400-405 04	—	405	30 in. 0-92 24 in. 0-225 20 in. 0-276	Opo	69	11-67
11642140600	445319093231501	203101	Edina municipal well 16	do	11-67	0-115 04 115-173 04 173-255 04 255-380 04 380-380 04	895	380	30 in. 0-215 20 in. 0-265	Opo	66	11-67
02812401003	445347002213901	200914	Edina municipal well 17	Keys	11-70	0-133 04 133-181 04 181-201 04 201-363 04 363-461 04	—	461 461	30 in. 0-196 24 in. 0-373	CJ	59	11-70
02812401003	445347002213901	200918	Edina municipal well 18	do	10-73	0-237 04 237-345 04 345-444 04	—	446	30 in. 0-150 24 in. 0-232 16 in. 0-365	CJ	61	10-73

PROVISIONAL RECORDS
Subject to Revision

PROVISIONAL RECORDS
Subject to Revision

U.S. GEOLOGICAL SURVEY
WATER RESOURCES DIVISION
702 POST OFFICE BUILDING
ST. PAUL, MINNESOTA 55101

Inventory Name	Inventory Number	Range Number	Volume No.	Page	Page	Page
	N	1				
	01	01				
	8	8				

I have no need, however, from Road Intersections or Street Address and City of Salt Lake Division

Sketch map of well location

NON-RESPONSIVE

[illegible]

IS REMARKS ELEVATION SOURCE OF DATA RM

Elevation = 214.2

מקור אמת

7 PROPERTY (OWNER NAME)
 Address **St. Louis Park Well #3**
2924 IDAHO AVE.

8 WELL IDENT (completed) **286** Date of Completion **August, 1959**

9 ☐ 1" hole end ☐ 4" opening ☐ 5" between ☐ 10" ring
☐ 2" hole end ☐ 3" air ☐ 6" ring ☐ 11" _____
☐ 3" hole end ☐ 4" air ☐ 7" power auger

10 USE ☐ Domestic ☐ Public Supply ☐ Industry
☐ Irrigation ☒ Municipal ☐ Commercial
☐ Test Well ☐ Air conditioning ☐ _____

11 CASING HEIGHT Above/Below HOLE DIAM
☐ 1" Black ☐ Threaded Surface _____ ft.
☐ 2" Galv ☐ Welded Drive Short Yes _____ No _____
☐ 3" _____ Weight _____ lbs ft
24 in to **103** ft Weight _____ lbs ft
 _____ in to _____ ft Weight _____ lbs ft
 _____ in to _____ ft Weight _____ lbs ft

12 SCREEN Or open hole from **103** ft to **286** ft
 Make _____
 Type _____ Dia _____
 Slot/Grate _____ Length _____
 Set between _____ ft and _____ ft FITTINGS
 _____ ft and _____ ft
 _____ ft and _____ ft

13 STATIC WATER LEVEL **50** ft ☒ Below land surface ☐ Above Date Measured _____

14 PUMPING LEVEL (Below land surface) **164** ft after _____ hrs pumping **1350** g.p.m.
 _____ ft after _____ hrs pumping _____ g.p.m.

15 WELL HEAD COMPLETION ☐ Pattern adapter ☐ Blow-out effort ☐ At least 12" above grade

16 Well grouted? ☐ Yes ☐ No Co Yds _____
☐ Seal Cement ☐ Bentonite ☐ _____
 Depth from _____ ft to _____ ft
 from _____ ft to _____ ft

17 Nearest sources of possible contamination _____ feet _____ direction _____ type
 Well disconnected upon completion? Yes ☐ No ☐

18 PUMP Date installed _____
☒ Not installed
 Manufacturer's Name _____
 Model Number _____ HP _____ Volts _____
 Length of drop pipe _____ ft capacity _____ g.p.m.
 Material of drop pipe _____
 Type ☐ Submersible ☐ L.S. Turbine ☐ Reciprocating
☐ Jet ☐ Centrifugal ☐ _____

Executive Business Agency

Larvae No.

Abstract

Signed

Authorized Representatives

— But?

Name of Librarian

Date _____

REPORT

Tack No.

Well No. 3

Town St. Louis Park

Date Started Machine No. State Minnesota

Date Completed August 1939 Owner Village

Location by the Tower Total Depth of Well

DIAMETER OF HOLE	24"				
Top of Pipe ^{above} Surface					
Bottom of Pipe below Surface	105'				
No. of Ft. of Pipe in the Hole					
No. of Ft. of Hole Drilled					

TEST	1	2	3	4	FORMATION	Thickness	Depth
Depth of the Hole	286				Drift	103	103
Depth to Water at Rest	72				Limerock	15	118
Depth to Water Pumping					Sandrock	112	230
Depth of Pump Pipe					Red Shale	15	245
Size of Cylinder					Shale & Sandrock	41	286
Length of Stroke							
Strokes per minute							
Gallons per minute							
Will well supply more?					12/15/51-From Vralsted's records.		
Was Strainer in Hole?					12/31/51-Static 44' with pumps on		
Was water clear?					Wells #1 & #2 running.		
Was well pumping sand?					Static level 63' with #3		
Hours putting in Pump					only running. Water level 85		
Hours Pumping							
Hours taking out Pump							
Hours Consumed							

STRAINER

Make		
Type of Metal		
Diameter O. D.		
Diameter I. D.		
Total Length		
Number		
Top of Screen below Surface		
No. of Ft. Exposed		
Bottom of Screen below Surface		
Was Str. swedged		
Did Sand come thru Str.		
Was Str. coarse enough		
Style of Fittings		

All measurements taken from

LAYNE-WESTERN COMPANY

OF MINNESOTA

FIELD REPORT OF COMPLETED WELL

Name of Job St. Louis Park, Minn. Date started 4/17/46
 Address No. 4 Date completed _____
NON-RESPONSIVE No. of days _____

LOG OF WELL

From	To	Material	From	To	Material
0	3	Dirt fill	291	355	Hard lime
3	76	Sand & gravel	355	398	Lime, milky cuttings
76	106	Platteville Lime.	398	445	Jordan sandstone
106	235	Soft St. Peter Sand.	445	455	Jordan Sandstone & shale, ^{hard}
235	277	Hard sandstone & shale	455	470	" "
277	291	Hard lime	470	490	St. Lawrence

Kind of plug in well none Static water level _____
 Depth of well - ground level to top of plug _____

MATERIAL LEFT IN WELL

	Opening	Length - feet	Diameter - inches	Material
Screen				
Inner casing		304'	18" O.D.	
Outer casing		89'10"	24" O.D.	

Was outer casing cemented _____ Amount _____
 Size of gravel used _____ in. to _____ in. Amount _____

TEST OF WELL

Hours Pumped		Yield gal. per min.	Water Level ft. below surface	Remarks
From	To			
9/18 4PM	9/19 4 PM	2500	82'	drawdown averages 53' length of airline 180' to top of bowls

Did well clear up yes Time to clear approx. 4 hours
 Date _____ Driller _____

REPORT

Tack No.

Well No. 4

Town St. Louis Park

Date Started Machine No. State Minnesota

Date Completed 4/7/46 Owner Village

Total Depth of Well

DIAMETER OF HOLE	24"	18"			
Top of Pipe ^{above} Surface					
Bottom of Pipe below Surface	89' 10"	304'			
No. of Ft. of Pipe in the Hole					
No. of Ft. of Hole Drilled					

TEST	1	2	3	4	FORMATION	Thickness	Depth
Depth of the Hole	490				Dirt Fill	0	3
Depth to Water at Rest	72				Sand & Gravel	73	76
Depth to Water Pumping	125				Platteville	30	106
Depth of Pump Pipe					St. Peter soft.	129	235
Size of Cylinder					Hard Sandstone & Shale	42	277
Length of Stroke					Hard Lime	73	355
Strokes per minute					Lime Lilky Cuttings	43	398
Gallons per minute	2500				Jordan Sandstone	47	445
Will well supply more?					Jordan & Shale hard.	10	455
Was Strainer in Hole?					Jordan Sandstone	15	470
Was water clear?					St. Lawrence	20	490
Was well pumping sand?							
Hours putting in Pump							
Hours Pumping							
Hours taking out Pump							
Hours Consumed							

12/15/51-Above from Vreelste's Record
12/31/51-Static 63'.

STRAINER

Make		
Type of Metal		
Diameter O. D.		
Diameter I. D.		
Total Length		
Number		
Top of Screen below Surface		
No. of Ft. Exposed		
Bottom of Screen below Surface		
Was Str. swedged		
Did Sand come thru Str.		
Was Str. coarse enough		
Style of Fittings		

All measurements taken from

REPORT

Tack No.

Well No. 5

Town St. Louis Park

Date Started 5/28/47

Machine No. State Minnesota

Date Completed 8/21/47

Owner Village

Total Depth of Well

DIAMETER OF HOLE	24"	20"			
Top of Pipe ^{above} Surface					
Bottom of Pipe below Surface	115'	305'			
No. of Ft. of Pipe in the Hole					
No. of Ft. of Hole Drilled					

TEST	1	2	3	4	FORMATION	Thickness	Depth
Depth of the Hole	465				Sand & Gravel	5	5
Depth to Water at Rest	87				Clay & Boulders	10	15
Depth to Water Pumping					Sand & Gravel	88	103
Depth of Pump Pipe					Coarse Gravel	6	109
Size of Cylinder					Lime	11	120
Length of Stroke					Rock & Shale	12	132
Strokes per minute					St. Peter	98	230
Gallons per minute					Shale & Rock	55	285
Will well supply more?					Shakopee Lime	122	407
Was Strainer in Hole?					Jordan Sand	58	460
Was water clear?					St. Lawrence	5	465
Was well pumping sand?							
Hours putting in Pump							
Hours Pumping							
Hours taking out Pump							
Hours Consumed							

15 Yds. cement used.

12/15/51-Above from Vralsted's record

12/31/51-Static 76' at 1200 GPM

Water drew down to 88'.

STRAINER

Make		
Type of Metal		
Diameter O. D.		
Diameter I. D.		
Total Length		
Number		
Top of Screen below Surface		
No. of Ft. Exposed		
Bottom of Screen below Surface		
Was Str. swedged		
Did Sand come thru Str.		
Was Str. coarse enough		
Style of Fittings		

All measurements taken from

LAYNE-WESTERN COMPANY
OF MINNESOTA

FIELD REPORT OF COMPLETED WELL

Name of Job St. Louis Park, Minnesota Date started 9/30/47
Address N. 6 Date completed 1/19/48
No. of days 73

LOG OF WELL

From	To	Material	From	To	Material
0	90	sand & gravel	480	482	St. Lawrence
90	122	Platteville lime			
122	127	Blue shale			
127	290	St. Peter sand - soft			
290	417	Shakopee lime			
417	480	Jordan sandstone			

Kind of plug in well none Static water level 60'
Depth of well - ground level to top of plug 482'

MATERIAL LEFT IN WELL

	Opening	Length - feet	Diameter - inches	Material
Screen				
Inner casing		303'	20" O.D.	welded
Outer casing		107'6"	24" O.D.	welded

Was outer casing cemented yes Amount 24 yards
Size of gravel used in. to in. Amount

TEST OF WELL

Hours Pumped		Yield	Water Level	Remarks
From	To	gal. per min.	ft. below surface	
Test of well		appears on another report		

Did well clear up Time to clear
Date 1/19/48 Driller Paul W. Shuey

REPORT

Tack No.

Well No. 6

Town St. Louis Park

Date Started 9/30/47

Machine No. State Minn.

Date Completed 1/19/48

Owner Village

NON-RESPONSIVE

Total Depth of Well

DIAMETER OF HOLE	24"	20"			
Top of Pipe ^{above} Surface					
Bottom of Pipe below Surface	107'6"	303'			
No. of Ft. of Pipe in the Hole					
No. of Ft. of Hole Drilled					

TEST	1	2	3	4	FORMATION	Thickness	Depth
Depth of the Hole	482				Sand & Gravel	90	90
Depth to Water at Rest	60				Platteville	32	122
Depth to Water Pumping					Blue Shale	5	127
Depth of Pump Pipe					St. Peter soft.	163	290
Size of Cylinder					Shakopee Lime	127	417
Length of Stroke					Jordan Sandstone	63	480
Strokes per minute					St. Lawrence	2	482
Gallons per minute							
Will well supply more?							
Was Strainer in Hole?					24 Yds. cement used.		
Was water clear?							
Was well pumping sand?					12/15/51-Above from Vraalsted's Record		
Hours putting in Pump					12/31/51-Static 55'. At 1200 GPM		
Hours Pumping					water crew down to 81'.		
Hours taking out Pump							
Hours Consumed							

STRAINER

Make		
Type of Metal		
Diameter O. D.		
Diameter I. D.		
Total Length		
Number		
Top of Screen below Surface		
No. of Ft. Exposed		
Bottom of Screen below Surface		
Was Str. swaged		
Did Sand come thru Str.		
Was Str. coarse enough		
Style of Fittings		

All measurements taken from

LAYNE - MINNESOTA CO.

FLORIDA 192.00

FIELD REPORT OF COMPLETED WELL

Name of Job St. Louis Park Date started 3/10/52
 Address NON-RESPONSIVE Date completed 5/9/52
No 7 No. of days 41

LOG OF WELL

From	To	Material	From	To	Material
0	75	Sand gravel & Boulders	380	420	Good Gordon Sand.
75	97	Platville Lime	420	430	Fine Sand & Shale
97	100	Shale	430	440	Coarse Jordan Sand
100	210	Saint Peter Sand.	440	446	St. Lawrence.
210	260	Shale & Sand			
260	380	Dolemite lime.			

Kind of plug in well none Static water level 58
 Depth of well - ground level to top of plug 446

MATERIAL LEFT IN WELL

Opening	Length - feet	Diameter - inches	Material
Screen <u>none</u>			
Inner casing	<u>274</u>	<u>20"</u>	<u>Welded</u>
Outer casing	<u>80</u>	<u>24"</u>	<u>Welded</u>

Was outer casing cemented Drove Amount

Size of gravel used in. to in. Amount
 Inner Casing Cemented 25 sacks plus 10 yds. Ready Mix.

TEST OF WELL

Hours Pumped		Yield gal. per min.	Water Level ft. below surface	Remarks
From	To			

Did well clear up Time to clear
 Date 5/12/52 Driller Paul W. Shuey

REPORT

Tack No.

Well No. 7

Town St. Louis Park

Date Started Machine No. State Minnesota

Date Completed Owner City

NON-RESPONSIVE

Total Depth of Well 446'

DIAMETER OF HOLE	24"OD	20"OD			
Top of Pipe ^{above} Surface					
Bottom of Pipe below Surface	80'	247'			
No. of Ft. of Pipe in the Hole					
No. of Ft. of Hole Drilled					

TEST	1	2	3	4	FORMATION	Thickness	Depth
Depth of the Hole	446				Drift	75	75
Depth to Water at Rest	58				Plattville Limerock	25	100
Depth to Water Pumping					St. Peter Sandrock	160	260
Depth of Pump Pipe					Shakopee	120	380
Gallons per minute					Jordan Sandrock	60	440
Will well supply more?					St. Laurence	6	446
Was Strainer in Hole?							
Was water clear?					25 sacks of cement		
Was well pumping sand?					10 yds. of ready mix		
Hours Pumping							

STRAINER

Make		
Type of Metal		
Diameter O. D.		
Diameter I. D.		
Total Length		
Number		
Top of Screen below Surface		
No. of Ft. Exposed		
Bottom of Screen below Surface		
Was Str. swedged		
Did Sand come thru Str.		
Was Str. coarse enough		
Style of Fittings		

~~XXXX~~

Above information from
Layne report and city.

All measurements taken from

REPORT

Tack No.

Town St Louis Park

Date Started 3/10/52

Machine No. State MINN

Date Completed 5/9/52

Owner Village

NON-RESPONSIVE

Total Depth of Well 446

DIAMETER OF HOLE	24"	20"			
Top of Pipe ^{above} Surface					
Bottom of Pipe below Surface					
No. of Ft. of Pipe in the Hole	<u>80'</u>	<u>274"</u>			
No. of Ft. of Hole Drilled		<u>446</u>			

TEST	1	2	3	4	FORMATION	Thickness	Depth
Depth of the Hole					<u>Drift</u>	<u>75</u>	<u>75</u>
Depth to Water at Rest	<u>58</u>				<u>Platteville</u>	<u>22</u>	<u>97</u>
Depth to Water Pumping					<u>Shale</u>	<u>3</u>	<u>100</u>
Depth of Pump Pipe					<u>St Peter</u>	<u>110</u>	<u>210</u>
Size of Cylinder					<u>Shale + Sand</u>	<u>50</u>	<u>260</u>
Length of Stroke					<u>Dalomite - Shakopee</u>	<u>120</u>	<u>380</u>
Strokes per minute					<u>Jordan</u>	<u>40</u>	<u>420</u>
Gallons per minute					<u>Fine Sand & Shale</u>	<u>10</u>	<u>430</u>
Will well supply more?					<u>Coarse - Jordan</u>	<u>10</u>	<u>440</u>
Was Strainer in Hole?					<u>Shale</u>	<u>6</u>	<u>446</u>
Was water clear?							
Was well pumping sand?							
Hours putting in Pump							
Hours Pumping							
Hours taking out Pump							
Hours Consumed							

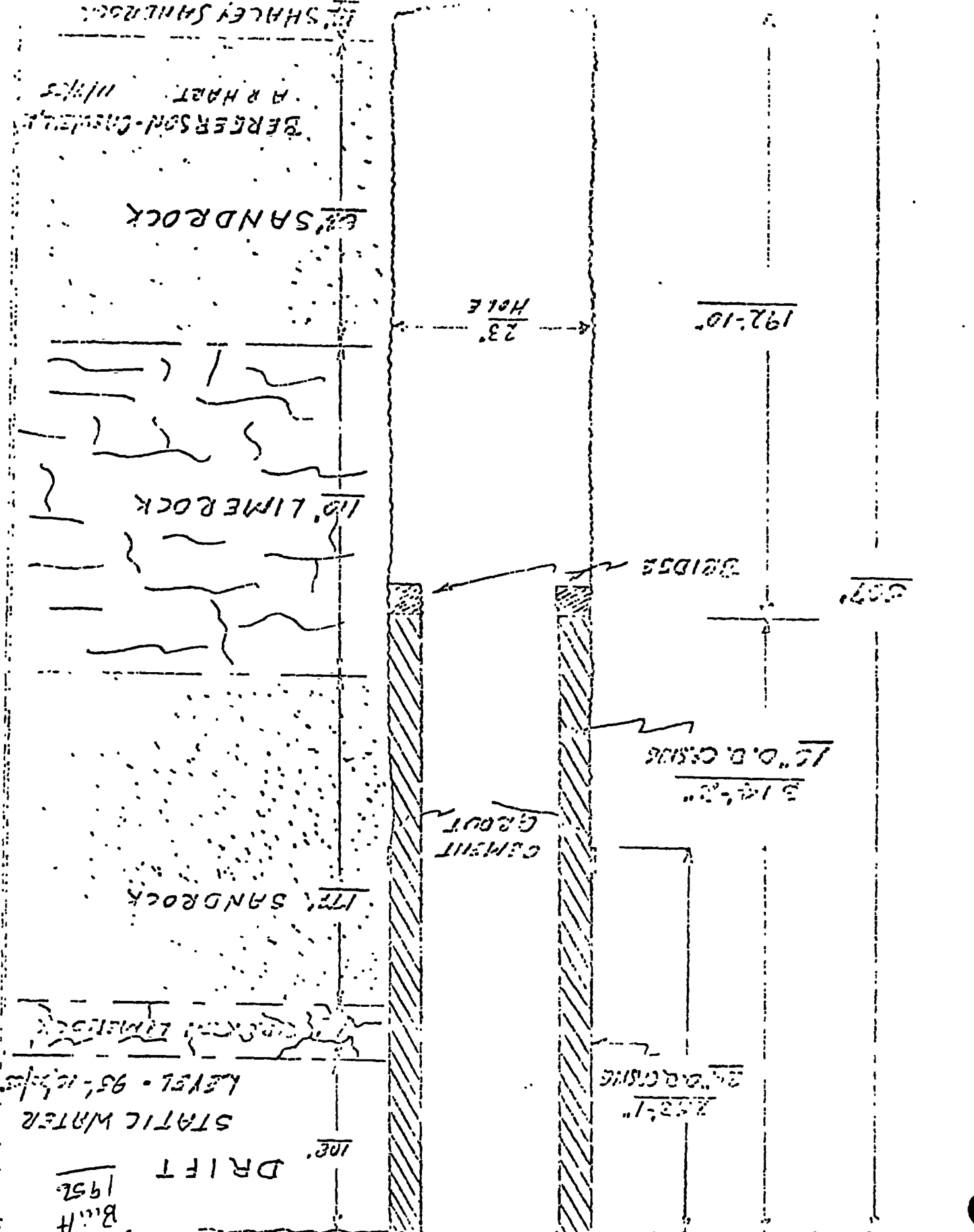
STRAINER

Make		
Type of Metal		
Diameter O. D.		
Diameter I. D.		
Total Length		
Number		
Top of Screen below Surface		
No. of Ft. Exposed		
Bottom of Screen below Surface		
Was Str. swedged		
Did Sand come thru Str.		
Was Str. coarse enough		
Style of Fittings		

El Floor of Pump Room.
194 + 710.3 = 904.3

All measurements taken from

WELL #8 - CITY OF ST. LOUIS PARK, MINN.



REPORT

Tack No.

Well No. 8

G. B. C. Inc

Town St. Louis Park

Date Started 6/10/55

Machine No. State Minnesota

Date Completed 11/2/55

Owner City

NON-RESPONSIVE

Total Depth of Well 507'

DIAMETER OF HOLE	24" O.D.	16" O.D.			
Top of Pipe ^{above} Surface	3'	3'1"			
Bottom of Pipe below Surface	250'1"	311'1"			
No. of Ft. of Pipe in the Hole	253'1"	314'2"			
No. of Ft. of Hole Drilled	507'				

TEST	1	2	3	4	FORMATION	Thickness	Depth
Depth of the Hole	507	507	507		Platform	3	3
Depth to Water at Rest					Yellow Clay, Rocks & Boulders	35	38
Depth to Water Pumping	143	115	111		Hard red clay & rocks	27	65
Depth of Pump Pipe					Brown gray clay & rocks	32	97
Gallons per minute	1750	1000	800		Sand & gravel (dirty)	11	108
Will well supply more?					Clay, rocks & broken limerock - Gravel & broken limerock-Platteville		
Was Strainer in Hole?						18	126
Was water clear?						177	303
Was well pumping sand?					St. Peter formation		
Hours Pumping					Yellow shale	6'	

STRAINER

Make		
Type of Metal		
Diameter O. D.		
Diameter I. D.		
Total Length		
Number		
Top of Screen below Surface		
No. of Ft. Exposed		
Bottom of Screen below Surface		
Was Str. swedged		
Did Sand come thru Str.		
Was Str. coarse enough		
Style of Fittings		

Sandrock & shale	47	
Sandrock	63	
Shale	17	
Sandrock (Hard)	43	
Shale & Sandrock	1	
Shakopee limerock (Hard)	110	413
Jordan formation:	82	495
Sandrock-Med. hard & clean	23'	
" Fine, hard, red	28	
" Very hard, shaly	18	
" Med. hard, white, coarse	4	
" Med. hard, white, fine	10	
Shaly Sandrock	12	507'

All measurements taken from Grade
EL 931.3'

10/25/55 Ira Vraalstad reports sand
content of water @ 1000 GPM -13 PPM
800 GPM -0.6 PPM

LAYNE - MINNESOTA CO.

FIELD REPORT OF COMPLETED WELL

Name of Job St. Louis Park, Minnesota Date started _____
 Address Well # 9 Date completed 6-6-56
 _____ No. of days _____

LOG OF WELL

From	To	Material	From	To	Material
0	69	Drift	345	380	Shakopee Limestone
69	120	Platteville Limestone	380	473	Jordan Sandstone
120	220	Shale and sandstone			
220	275	Shale			
275	339	Shakopee Limestone			
339	345	Red Sandstone			

Kind of plug in well Pressure Grouted Liner Static water level 70'
 Depth of well - ground level to top of plug _____

MATERIAL LEFT IN WELL

	Opening	Length - feet	Diameter - inches	Material
Screen				
Inner casing		289'	16"	Steel
Outer casing		81'	24'	Steel

Was outer casing cemented _____ Yds _____ Amount 2414 Bags
 Size of gravel used _____ in. to _____ in. Amount _____

TEST OF WELL

Hours Pumped		Yield gal. per min.	Water Level ft. below surface	Remarks
From	To			
				See Pump test report

Did well clear up _____ Time to clear _____

Date 6-8-56 Driller Wayne La Fontaine

E. H. Renner & Sons

WELL DRILLING FOR FOUR GENERATIONS
8300 Industry Ave. N. W., Anoka, Minn. 55303, (612) 427-6100

WELL LOG #10

MAP CODE _____

Date Started _____ 19 55

Owner or Contractor City of St. Louis Park

Job Location 29th and Idaho area

NON-RESPONSIVE

Lot _____ Block _____ City St. Louis Park County Hennepin State of Minnesota

Well: ☒ Cable Tool ☒ Rotary ☐ Driven 106' Driller Key's Well Drilling Co.

Cased with 16 inch ☒ PE ☐ T&C 315'-6" Ft. Total Depth of Well 500 Ft from grade

Feet of Open Hole 185 Finished in Jordan Sandstone Static Water Level 104 Ft

Tested at 2055 gallons per min Drawn down of 100 feet
1060 57

Screen
Size _____ dia. _____ ft Make _____ Slot or Gauge _____

Pump:
Make _____ HP. _____ Volts _____ Phase _____ Type _____ Tank _____

Motor Serial No _____ Pump Serial No _____ Drop Pipe _____ feet

Size _____ Capacity of pump _____ G.P.M. Date Installed _____

Pitless Adapter: Make _____ Offset _____ ft. Material _____ Size _____ inch

Kind of Formation	Color of Formation	Started Depth	Ended Depth	Total Thickness of Formation	Remarks
Sand & Gravel		0	85	85	
Clay		85	103	18	Well is grouted from 315' to surface 1025 bags cement
Platville		103	125	22	
St. Peter		125	290	165	
Shakopee Dolomite		290	409	119	
Jordan		409	500	91	

REPORT

Tack No.

Well No. 10

Town St. Louis Park

Date Started..... Machine No..... State Minnesota

Date Completed..... Owner..... City of St. Louis Park

Location..... Total Depth of Well.....

DIAMETER OF HOLE	24"	16"			
Top of Pipe ^{above} Surface.....					
Bottom of Pipe below Surface.....	106	315			
No. of Ft. of Pipe in the Hole.....					
No. of Ft. of Hole Drilled.....					

TEST	1	2	3	4	FORMATION	Thickness	Depth
Depth of the Hole.....					Drift		108
Depth to Water at Rest.....	104				Platteville		125
Depth to Water Pumping.....	200				St. Peter		290
Depth of Pump Pipe.....					Shakopee/Oneota		290
Gallons per minute.....	2000				Jordan		409
Will well supply more?.....					St. Lawrence		500
Was Strainer in Hole?.....							
Was water clear?.....							
Was well pumping sand?..							
Hours Pumping.....							

STRAINER

Make.....			
Type of Metal ...			
Diameter O. D.....			
Diameter I. D.....			
Total Length.....			
Number.....			
Top of Screen below Surface.....			
No. of Ft. Exposed.....			
Bottom of Screen below Surface.....			
Was Str. swedged.....			
Did Sand come thru Str.....			
Was Str. coarse enough.....			
Style of Fittings.....			

All measurements taken from

REPORT

Tack No. 258 Green

Well No. 11

By Bergerson-Caswell Inc. Town St. Louis Park

Date Started 6-13-60 Machine No. State Minnesota

Owner City of St. Louis Park

NON-RESPONSIVE

Total Depth of Well 1093'

DIAMETER OF HOLE	24"	16"			
Top of Pipe ^{above} Surface	1	-9'8"			
Bottom of Pipe below Surface	102	880			
No. of Ft. of Pipe in the Hole	103	870'4"			
No. of Ft. of Hole Drilled	777	213'			

TEST	1	2	3	4	FORMATION	Thickness	Depth
Depth of the Hole	124.5		124.5		Drift	101	101
Depth to Water at Rest	121	121	121	121	Plattville Limerock	19	120
Depth to Water Pumping	124	124	124	124	St. Peter Sandrock	168	288
Depth of Pump Pipe					Shakopee-Oneota limerock	120	408
Gallons per minute	1200	115	1200	1200	Jordan sandrock	97	505
Will well supply more?	No	No	No	No	St. Laurence-limerock-shale	25	530
Was Strainer in Hole?	No	No	No	No	Franconia-hard, sticky		
Was water clear?	No	No	No	No	green shale	153	683
Was well pumping sand?	No	No	No	No	Dresbach	272	955
Hours Pumping	1.5	1.5	1.5	1.5	Gailesville-clean hard SR		

STRAINER

Make			
Type of Metal			
Diameter O. D.			
Diameter I. D.			
Total Length			
Number			
Top of Screen below Surface			
No. of Ft. Exposed			
Bottom of Screen below Surface			
Was Str. swedged			
Did Sand come thru Str.			
Was Str. coarse enough			
Style of Fittings			

805' to 813' (8')		
green shale		
813 to 817 (4')		
Sandrock & shale		
817 to 853 (36')		
Mt. Simon		
hard sandrock and shale		
853 to 955 (102')		
Hinckley	123	1078
Pinkish red sandrock some		
shale 955' to 1050' (95')		
Hard clean coarse S.R.		
1050' to 1078' (28')		
Red Clastic	15	1093'

All measurements taken from platform-approximately 12" above perm. grade.

SHOT WELL #1--50# @ 1070'
#2--50# @ 1060'
#3--50# @ 1050'
#4--50# @ 1030'
#5--50# @ 1010'

Calculated on number of bailers removed and bailer fill--est. removed 225 1/2 Cu.Yds.

182 after shooting & bailing & testing pumping pulled pump and found hole filled to 1024'

384 Bailed clean and reinstalled test pump.

12/5/60 Mailed Minn. Conserv. Dept. Well log sheet jwm

WELL RECORD

KEYS WELL DRILLING COMPANY WATER PRODUCERS

SAINT PAUL, MINNESOTA

Owner ST. LOUIS PARK,

Date Completed August, 1963

NON-RESPONSIVE

Driller Kemper

Well No. 18 Size 30x24x16 Total Depth 1095 Type _____

DRILLERS LOG

0 ' to 96 ' Drift
96 ' to 127 ' Flatville
127 ' to 132 ' Shale (Glenwood)
132 ' to 292 ' St. Peter
292 ' to 427 ' Shakopee
427 ' to 505 ' Jordan
505 ' to 550 ' St. Lawrence
550 ' to 695 ' Franconia
695 ' to 725 ' Ironton
725 ' to 745 ' Dressbach (Galeville)
745 ' to 832 ' Dressbach (Eau Claire)
832 ' to 983 ' Dressbach (Mt. Simon)
983 ' to 1095 ' Hinckley
_____ ' to _____ ' _____

PERMANENT PUMP DATA

Mfg. _____ Type _____ Serial No. _____
Capacity _____ GPM _____ TDH _____
Motor Make _____ Type _____
_____ H. P. _____ Volts _____ Ph. _____ RPM _____
_____ ft. _____ in Col. pipe _____ in. Shaft _____
_____ ft. _____ in Bowls _____ Stages _____ Type _____
_____ ft. _____ in suction pipe & _____
_____ ft. Total Length of Pump _____
_____ ft. _____ in. drop pipe & _____ No. Cable _____
_____ ft. _____ in. air line _____
_____ in. Pitless _____ ft. bury _____ in outlet _____

WELL MATERIALS

99 ' of 30 " diameter of Outer Casing
160 ' of 29 " diameter of Open Hole
270 ' of 24 " diameter of Inner Casing
825 ' of 23 " diameter of Open Hole
900 ' to 16 " liner grouted in with:
Mix grout 1860 (Sacks)
_____ " diameter _____ Screen

RECORD OF TEST PUMPING

Static Water Level 245 ft. from _____
863 GPM 86 D.D. 11 Hours
1012 GPM 95 D.D. 8 Hours
1235 GPM 117 D.D. 8 Hours
1218 GPM 114 D.D. 11 Hours
1455 GPM 127 D.D. 18 Hours
1585 GPM 128 D.D. 4 Hours
1711 GPM 143 D.D. 4 Hours
1795 GPM 154 D.D. 5 Hours

Remarks: 580' of Hinckley sandrock removed
after blasting & bailing.

1863 GPM 157' D.D. 11 Hours
2000 156' 2
1500 122'6" 13
1300 108' 1
1100 93' 1

LAYNE-MINNESOTA CO.

FIELD REPORT OF COMPLETED WELL

Name of Job St. Louis Park Well No. 13 Date started Oct. 1, 1963
NON-RESPONSIVE Date completed July 1, 1964
 No. of days _____

LOG OF WELL

From	To	Material	From	To	Material
386'	460'	Gordon Sand	770'	778'	Mt. Simon Sandstone
460'	490'	St. Lawrence	778'	917'	Hit layers of 1' to 2' thick shale in sand formation
490'	655'	Franconia			
655'	714'	Dresbach	917'	1040'	Hinkley Sandstone
714'	770'	Hard rubber shale	1040'	1045'	Red Clastic Formation filled Lt back in again

Method of drilling _____ Rig used _____ Diam. of drill hole _____ in.

Was outer casing cemented _____ Method _____ Amount cement _____

Depth of well - from ground level _____ ft. - from top of casing _____ ft. Static _____ ft.

MATERIAL LEFT IN WELL

	Opening	Length - feet	Diameter - inches	Material
Screen				
Inner casing				
Outer casing				

Underreamed from _____ ft. to _____ ft. Diameter _____ in. Method _____

Size-sizes-of gravel 1/4 by 1/2 Rock Backfill Amount 33 yards

Well shot at _____ ft. to _____ ft. depth Number _____ Size _____ lb. Material removed _____ yd.

WELL TEST

Hours Pumped		Yield gal. per min.	Water Level - ft. below surface	Drawdown feet	Remarks
From	To				

Time to clear _____ Specific Capacity _____ g.p.m./ft. d.d.

Date July 1, 1964 Driller Gordon Hollen

REPORT

Tack No.

Well No. 14

Town St. Louis Park

Date Started 8/27/64

Machine No. State Minn.

Date Completed

Owner City of St. Louis Park

NON-RESPONSIVE

Total Depth of Well 485'

DIAMETER OF HOLE	30"	24"	16"		
Top of Pipe above Surface	-10'	0	0	press. grouted betwe	
Bottom of Pipe below Surface	94'	253'	389'	164' - 24' & 24' &	
No. of Ft. of Pipe in the Hole	84'			30" (710 sa	
No. of Ft. of Hole Drilled	159'	137'	96'		

TEST	1	2	3	4	FORMATION	Thickness	Depth
Depth of the Hole	485	485	485	485	Platform	3	3
Depth to Water at Rest	80	80	80	80	Glacial drift	91	94
Depth to Water Pumping	108	113	119	129	Plattville limerock	4	98
Depth of Pump Pipe					Glenwood shale	3	101
Gallons per minute	600	700	800	1000	St. Peter sandrock	164	265
Will well supply more?	yes	yes	yes	yes	Shakopee/Oneota limerock	110	485
Was Strainer in Hole?	no	no	no	no	Jordan sandrock	110	485
Was water clear?	yes	yes	yes	yes	Hard-med., clean-coarse		
Was well pumping sand?					375-410		
Hours Pumping PPM	4.0	5.0	9.0	12.5	Very hard - red.		

STRAINER

Make		
Type of Metal		
Diameter O. D.		
Diameter I. D.		
Total Length		
Number		
Top of Screen below Surface		
No. of Ft. Exposed		
Bottom of Screen below Surface		
Was Str. swedged		
Did Sand come thru Str.		
Was Str. coarse enough		
Style of Fittings		

Hard shaley
420-440
Hard-fine-tan-poor
440-450
Hard-fine, white, tan, poor
450-475
Hard, green shaly, fine
475-485

Jordan sandrock was shot -
removed 147 cu. yds. sandrock.

All measurements taken from grade plus 3'
El. 905' plus or minus

Tack No. _____
 Well No. 15
 Date Started 5/22/69 Machine No. _____ State Miss
 Date Completed 10/24/69 Owner City of St. Louis Park
 Location _____ Total Depth of Well _____

DIAMETER OF HOLE	30	24			
Top of Pipe above Surface					
Bottom of Pipe below Surface	102	398			
No. of Ft. of Pipe in the Hole					
No. of Ft. of Hole Drilled	297	105			

TEST	1	2	3	4	FORMATION	Water	De.
Depth of the Hole					Glacial drift	102	102
Depth to Water at Rest					Plattville limestone	22	124
Depth to Water Pumping					St. Peter sandrock	164	288
Depth of Pump Pipe					Shakopee/Onota limestone	114	402
Gallons per minute					Jordan sandrock	80	482
Will well supply more?					St. Lawrence shale	21	503
Was Strainer in Hole?							
Was water clear?							
Was well pumping sand?							
Hours Pumping							

STRAINER

Make	
Type of Metal	
Diameter O. D.	
Diameter I. D.	
Total Length	
Number	
Top of Screen below Surface	
No. of Ft. Exposed	
Bottom of Screen below Surface	
Was Str. swedged	
Did Sand come thru Str.	
Was Str. coarse enough	
Style of Fittings	

Well shot & bailed
 removed 182 cu. yd.

All measurements taken from Grade

117- Water level 21.5 ft. below ground

TRI-STATE DRILLING CO.

Owner ST. LOUIS PARK**NON-RESPONSIVE**Well Designation Deep Well No. 16Total Depth 500 feet.

DRILLER'S LOG

<u>0</u> ' to <u>60</u> ' <u>sand & gravel</u>
<u>60</u> ' to <u>80</u> ' <u>clay & boulders</u>
<u>80</u> ' to <u>105</u> ' <u>coarse sand & gravel</u>
<u>105</u> ' to <u>118</u> ' <u>broken limestone</u>
<u>118</u> ' to <u>128</u> ' <u>platteville limestone</u>
<u>128</u> ' to <u>258</u> ' <u>St. Peter sandstone</u>
<u>258</u> ' to <u>294</u> ' <u>red shale</u>
<u>294</u> ' to <u>410</u> ' <u>Shakopee limestone</u>
<u>410</u> ' to <u>495</u> ' <u>Jordan sandstone</u>
<u>495</u> ' to <u>500</u> ' <u>St. Laurance shale</u>
<u> </u> ' to <u> </u> ' <u> </u>
<u> </u> ' to <u> </u> ' <u> </u>
<u> </u> ' to <u> </u> ' <u> </u>
<u> </u> ' to <u> </u> ' <u> </u>
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<u> </u> ' to <u> </u> ' <u> </u>
<u> </u> ' to <u> </u> ' <u> </u>
<u> </u> ' to <u> </u> ' <u> </u>

TEST PUMPING DATA

Static water level 125 feet. Pumped at 2,000 g.p.m.with 238 foot level 2 P.P.M. sand at1200 G.P.M.Date completed 7/31/73Driller Frank BerthiaumeWell Type: ☒ Rock☐ Screen☐ Gravel Packed

WELL MATERIALS

410 ft. 30 in. diam. outer casing425 ft. 24 in. diam. liner pipe ft. in. diam. screenScreen type Remarks: Well liner grouted in.Jordan sandstone was developed byblasting & air surging & bailing.

PERMANENT PUMP DATA

Mfg. Model Serial No. Type h.p. Motor, V, Ph. ft. setting in. shaft in. col. pipeRemarks:

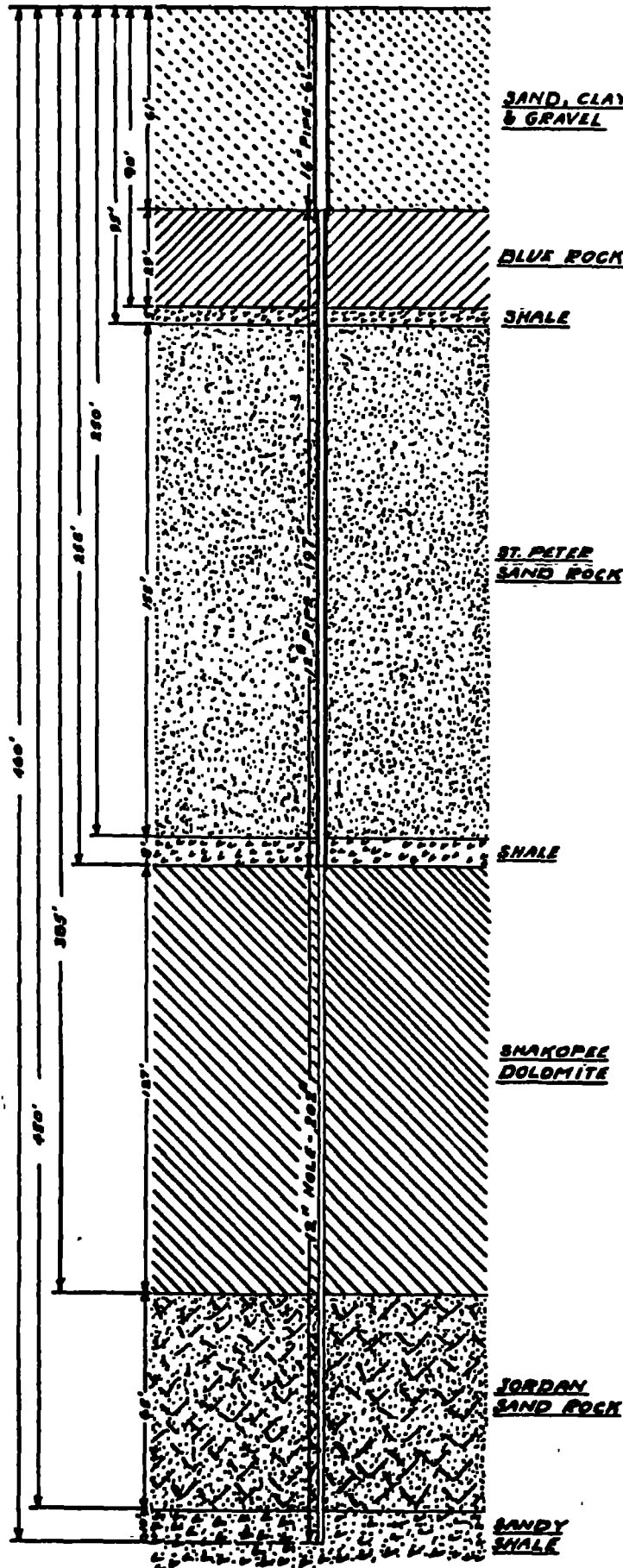
COUNTRY CLUB DISTRICT SERVICE CORPORATION WELL

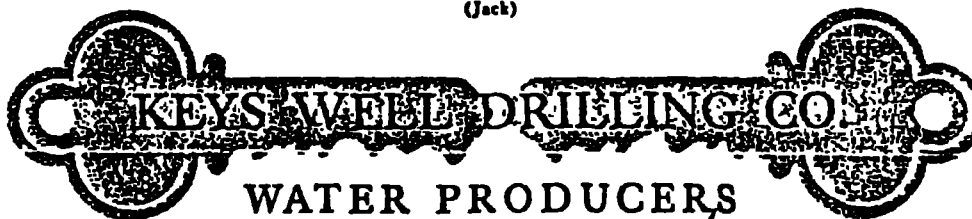
DRILLED IN NOVEMBER 1935

#2 Woodlake

EDIN A

Well
#2





Elkhurst 4993
Midway 8149

NON-RESPONSIVE

July 7, 1954

LOG OF WELL

VILLAGE OF EDINA, MINNESOTA

24" x 16" Well - Depth 505 feet - Water level 90 feet

96'6" of 24" Pipe

316' of 16" liner grouted in with $31\frac{1}{2}$ cu. yds of grout

115' of 12" G.W.I pipe slotted, gravel packed

Log of Well:

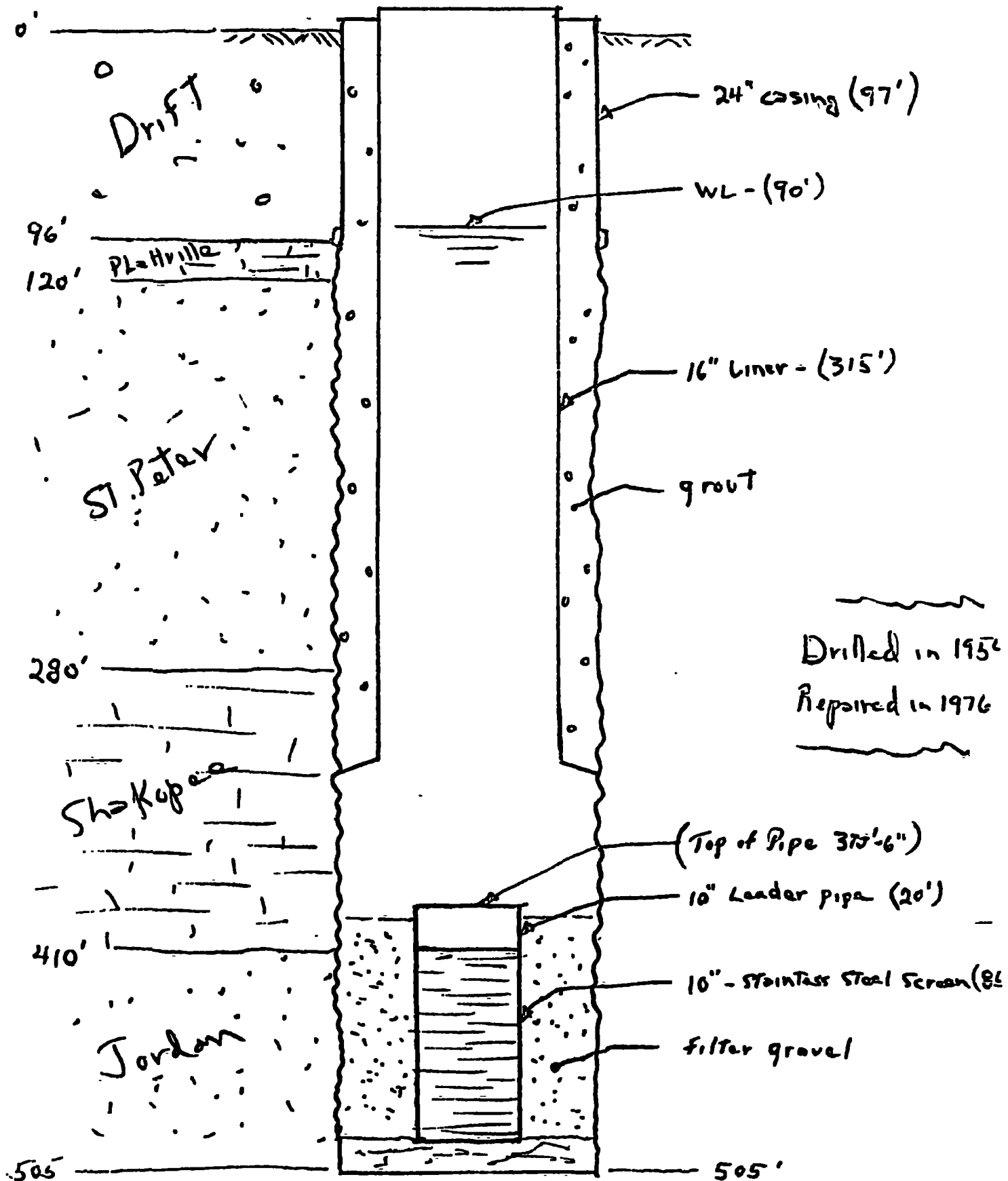
0 -	2	Pipe above ground
2 -	96	Yellow clay (sandy)
96 -	112	Limerock
112 -	120	Soapstone
120 -	280	St. Peter
280 -	410	Shakopee
410 -	495	Jordan
495 -	505	Shale

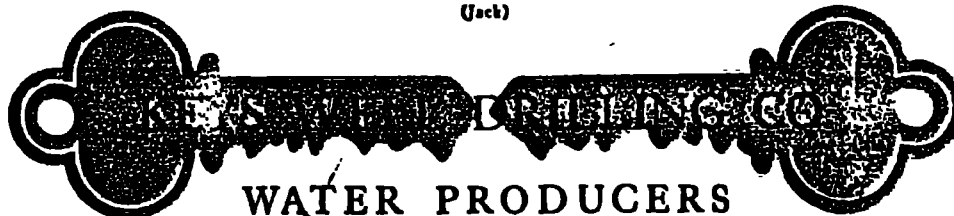
390 - FT. TOP OF SCREEN

Pumped:

1656	G.P.M.	-	75'	D.D.
1823	G.P.M.	-	70'	D.D.
1599	G.P.M.	-	60'	D.D.
1284	G.P.M.	-	48'	D.D.

WELL # 6 EDINA, Minn.





WATER PRODUCERS

Capital 7-6639

Capital 7-6630

NON-RESPONSIVE

*Sherwood Floor
EIV 853.62*

LOG OF WELLVILLAGE OF ELMA, MINNESOTAWELL #7

24" x 16" Well - Depth 547 feet - Water level 112 ft.

140' 6" of 24" Pipe

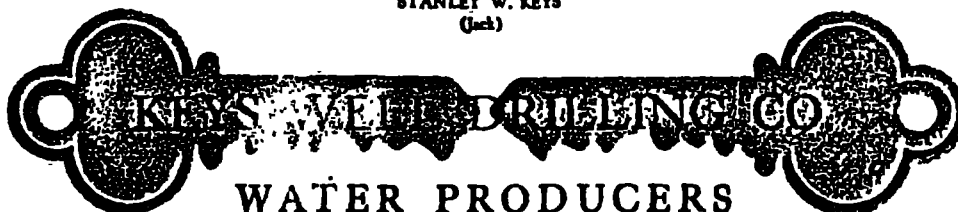
350' of 16" liner grouted in with 463 sacks cement in 1-1 mix

State 143 - 8/23/62

Tested: 1240 GPM - 25' DD
 1471 GPM - 36' DD
 1809 GPM - 47' DD

Log of Well:

0 - 18 Clay
 18 - 35 Sand and gravel
 35 - 78 Clay
 78 - 132 Sand
 132 - 159 Limerock
 159 - 162 Souderton
 162 - 290 Sandrock
 290 - 324 Sandrock and Shale
 324 - 453 Shakopee
 453 - 545 Jordan
 545 - 547 Shale



RECEIVED
MAY 25 1964

STANLEY
W. KEYS CO.

Telephones: 646-7871
646-7872

NON-RESPONSIVE

WELL NO. 13
Belmore Park
Edina, Minnesota

24" x 16" Well 496' Deep S.W.L. 96' 7"

109' - 24" Drive Pipe
387' - 23" Open Hole
429' - 16" Liner grouted in with 44 yds. of Grout

Blasted and Bailed Well for 157½ Hours

1st TEST

1000 G.P.M. - 37' D.D.
1500 G.P.M. - 51'1" D.D.
1700 G.P.M. - 60'3" D.D.
2000 G.P.M. - 75'4" D.D.

87 Hours

BAILED WELL

101 Hours

PUMP, IN & OUT

22½ Hours

2nd TEST

2000 G.P.M. - 53'10" D.D.
1500 G.P.M. - 41'3" D.D.
1000 G.P.M. - 30' D.D.

42½ Hours

BAILED HOLE TO BOTTOM

33½ Hours

444½ Hours

LOG:

0 - 2 Pipe above
2 - 41 Sand
41 - 60 Sandy Clay
60 - 81 Sand
81 - 106 Sandy Clay
106 - 121 Plattville
121 - 125 Soapstone
125 - 294 St. Peter
294 - 414 Shakopee
414 - 496 Jordan
496 - St. Lawrence

Well #13

LAYNE-MINNESOTA CO.

FIELD REPORT OF COMPLETED WELL

Name of Job Edina Well No. 15

Date started _____

NON-RESPONSIVE

Date completed 11/6/67

No. of days _____

LOG OF WELL

ft.		Material	ft.		Material
From	To		From	To	
0	91	Sand & Clay	260	265	Hard shale, blue
91	111	Platteville rock	265	400	Rock, Shakopee
111	205	St. Peter Sandstone	400		Jordan Sandstone-shaley sand
205	210	Shale & sand mix, hard			
210	260	Shale & sand mix.			

Total - 92' 4"

Method of drilling Cable tool Rig used 28L Diam of drill hole 30 in

Was outer casing cemented yes Method Pump Amount cement 27 yds.

Depth of well - from ground level 405 ft. - from top of casing 69 ft. Static 69 ft.

MATERIAL LEFT IN WELL

	Opening	Length - feet	Diameter - inches	Material
Screen		275' 10"	20" casing	3/8"
Inner casing		92' 4"	30" casing	3/8"
Outer casing		225' 3"	24" casing	3/8"

Under reamed from _____ ft. to _____ ft. Diameter _____ in. Method _____

Size-sizes-of gravel _____ Amount _____

Well shot at _____ ft. to _____ ft. depth Number _____ Size _____ lb. Material removed _____ yd

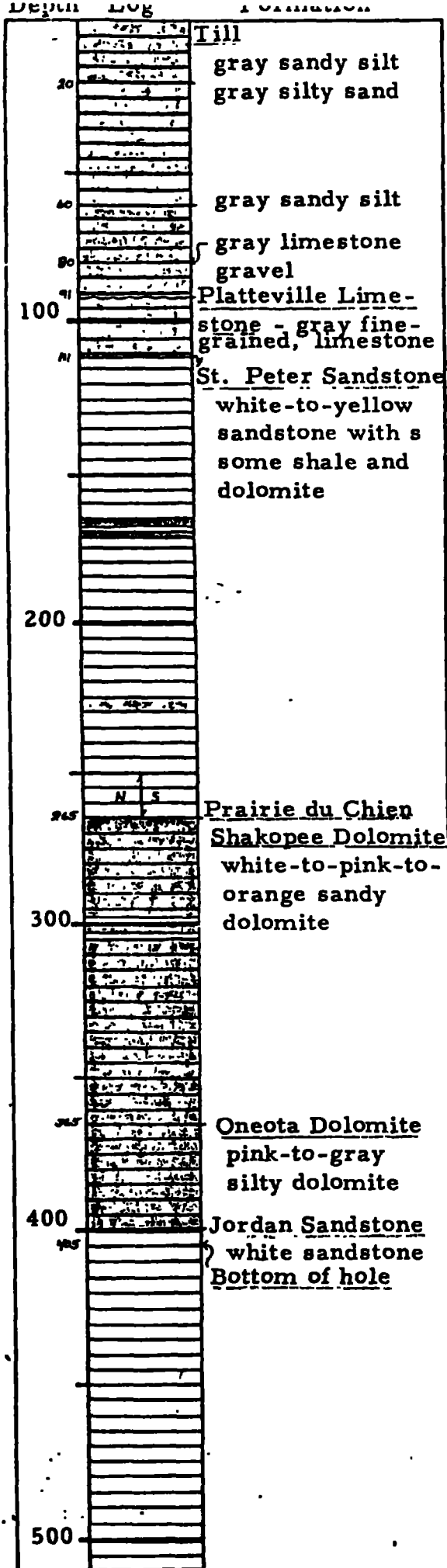
WELL TEST

Hours Pumped		Yield gal. per min.	Water Level- ft. below surface	Drawdown feet	Remarks
From	To				
3 PM	10 PM	1200	110'	41'	Pump lot of sand & dirty water
10 PM	10 AM	2000	138'	69'	Pumping clear now & less sand
10 AM	Noon	1800	126'	57'	Least sand at this rate.
1 PM	6 PM	1500	117'	48'	No sand & clear.

Time to clear 2 days Specific Capacity 1800 g.p.m./ft. d.d. 70'

Date 11/6/67
6 bags cement for bottom plug.

Driller /s/ Gordon Hollen



Minnesota Geological Survey Minneapolis, Minnesota			
Name Edina #15		State Minnesota	
Town Edina		County Hennepin	Loc.
Contractor Driller Layne-Minnesota		Sec. 29 dbb	
Drilling Dates Completed 11/6/67		T.	N., R. W.
Casing Record Screen - 275' 10"			
Inner casing 92' 4"			
Outer casing 225' 3"			
S. W. L. 69 ft.	G. P. M. 1800	D. D. 70'	
Remarks		Elev. 895 ± 5 ft.	
		T. D.	
Logged by G. S. Austin		M. G. S. No. 434	

Explanation
of Colors

- Soil
- Loess, Silt on Siltstone
- Drift
- Sand & Gravel
- Shale
- Sandstone
- Limestone
- Dolomite
- Clay
- No, Samples

WELL LOG STATEMENT

File No. 0-1
Well No. 117-21-19d6d

PORT PROMPTLY TO DIRECTOR, DIVISION OF WATERS, STATE OFFICE BLDG., ST. PAUL 1, MINN.

203198
Location of Well

Hopkins Well #3

Locate Well on
Plan of Section

NON-RESPONSIVE

County

City or Town

Describe Further by Lot, Block, Nearest Highway, Street and Number

28-33

Monk Ave & St. Louis Rd

Drilled for:

1121 2nd St. N.E. Driller

Address

Address

117-21-19d6d Addl.

Elev. 915±5'

Date of Completion

1948

Date of Test

Site

Upland, Valley, Hillside, Etc.

Type of Well

Dug, Driven, Bored, Drilled

Drill Rig Used

Solid Tool, Jet, Rotary

Diameter: Top

24"

Bottom

20"

Depth of Well

775'

Ground Elevation

910±

Sea Level Datum or Give Distance Above

or Below R. R., Highway, Lake, Etc.

Height of Casing Above Ground

Quality of Water

(Hard or Soft, Fresh or Salty, Etc.)

Temperature of Water

Was Laboratory Analysis Made?

For What Purpose Will Water Be Used?

Is Well Pumped?

Pump Capacity

4250 GPM

Was Well Sealed on Completion?

Does Well Overflow Without Pumping?

Yes or No

Natural Flow

GPM

What Pressure, or Head, at Ground Level?

Principal Aquifer Penetrated

Jordan S.S.

Duration of Test

Hrs.

Min.

104-B

Rate of Pumping

Static Water Level

GPM

Ft.

Water Level While Pumping

Ft.

Drawdown

Ft.

Time Required for Recovery

Expected Average Yield

Gal. per day

If Other Tests were Made, Give Details on Another Sheet.

Were Measurements Made of Effect on Other Nearby Wells During Test? Give Details.

No casing record

Aquifer unknown

(Fill Out Both Sides of Form)

WELL LOG

915

Geologic Formations Kind, Color, Hard or Soft	Thickness of Formation	Depth in Feet		Casing Diam.	Water Conditions Found
		From	To		
Clay		1	5		CLAY
Drift } 5 ft gravel		5	45		PLTS SAND, GRVL
drift } 5 ft g.		45	80		T/835 SAND, GRVL
Plattin L.S.		80	110	OP	T/905 OPVL LMSN
Blue shale		110	116	OG	T/999' OGWD SHLE
Shale & L.S.		116	145	OSP	240 116 SNDS
St. Peter S.S.		145	225		OSTP ²⁴ SNDS
Red shale Red shale		225	240		1675' 15 SHLE
Shale & Gravel } Green shale & L.S.		240	276	OP	SHLE, DLMT
Hard L.S.		276	396		OPDC DLMT
L.S.		396	460		DLMT
Sandy shale		460	475		CJDN SNDS

COPIED

Indicate Size, Type, & Location of Any Screens, Gravel Packs, Grouting, or Other Development

I hereby certify that, to the best of my knowledge, the data presented in this statement is a true and correct representation of conditions encountered in the construction of this well.

Dated at _____ this _____ day of _____, 19__.

(Firm Name) _____

By _____

Title _____

**MIDWEST
UNDERGROUND
INSPECTIONS**

WELL NO. 3 DATE Oct. 22, 1979
OWNER Hopkins, Minnesota
DRILLING FIRM Layne Minnesota
TYPE OF CASING Steel SIZE 16"
CASING LENGTH _____ YEAR INSTALLED _____
VIDEO TAPE NO. 1

[illegible]

WATER WELL RECORD
Minnesota Statutes 168A.07-.09

MINNESOTA UNIQUE WELL NO.

Water Sample

112228

Hennepin

NE

224

117N

22W

City of Hopkins

Hopkins, Minnesota

7 and Co. Rd. 18 - Hopkins #6

Sketch map of well location.

1. WELL DEPTH (completed)

545

Date of Completion

9/30/77

2. ☒ Cable tool ☐ Power ☐ Driven ☐ Dig
☐ Sollow rod ☐ Air ☐ Bored ☐
☐ Rotary ☐ Jetted ☐ Power Auger

3. USE

- ☐ Domestic ☒ Public Supply ☐ Industry
☐ Irrigation ☐ Air Conditioning ☐ Geothermal
☐ Test well ☐

4. CASING

Material ☐ Welded ☒ Surface 2
Black ☐ Galv. ☐
30 in. to 132 ft. depth
24 in. to 354 ft. depth
in. to ft. depth
Drive Shoe Type No

5. SCREEN

Type NONE

Or open hole

from 354 ft. to 545 ft.

Type

Dia.

Slot/Gauge

Length

Set between

ft. and

ft.

ft. and

ft.

ft. and

ft.

9. STATIC WATER LEVEL

147

ft. ☒ below ☐ above

Date Measured 9/29/77

10. TEST OF WELL (10 min. or 1 hour)

150

ft. water 7.516 ft. pumping 3000

ft. after

hrs. pumping

11. WELL CAPTION

- ☐ Fitness adapter ☐ Insect effect ☒ At least 12" above ground

12. WELL PROTECTED

☒ Yes ☐ No

Cv. Yds. 50

☒ Heat cement☐ Bentonite☐

Depth: from 0 ft. to 356 ft.

from ft. to ft.

13. Nearest source of possible contamination

feet

direction

Well disinfected upon completion? Yes ☒ No ☐

14. PUMP

Date installed

☒ Not installed

Manufacturer's Name

Model Number

HP

Volts

Length of drop pipe ft. capacity

Material of drop pipe

- Type: ☐ Submersible ☐ U.S. Turbine ☐ Reciprocating
☐ Jet ☐ Centrifugal ☐

15. WATER WELL CONTRACTOR'S CERTIFICATION

This well was drilled under my jurisdiction and this report is true to the best of my knowledge and belief.

Bergerson-Caswell Inc. 27058

License Number

License No.

5115 Industrial St., Maple Plain, MN.

E. R. Henrich 10/4/77

E. R. Henrich

Date of Issue

WELL RECORD

MEYER'S WELL DRILLING COMPANY

WATER PRODUCERS

SAINT PAUL, MINNESOTA

Owner VILLAGE OF MINNETONKA

Date May 2, 1967

NON-RESPONSIVE

Driller Sittig

Well No. 6 Size 24 x 20 x 15 Total Depth 485' Type Jordan

DRILLERS LOG

0 ' to 101 ' Drift
101 ' to 117 ' Limerock
117 ' to 133 ' Shale
133 ' to 213 ' Sandstone (sandy)
213 ' to 231 ' Shale
231 ' to 312 ' Sandstone (sandy)
312 ' to 322 ' Shakopee (sandy)
322 ' to 392 ' Shakopee (sandy)
392 ' to 435 ' Jordan (sandy)
435 ' to 442 ' Jordan (shale)
442 ' to 485 ' Jordan
485 ' to 485 ' Shale
' to '
' to '

PERMANENT PUMP DATA

Mfg. Type Serial No.
Capacity GPM TDH
Motor Make Type
 H. P. Volts Ph. RPM
 ft. in Col. pipe in. Shaft
 ft. in Bowls Stages Type
 ft. in suction pipe &
 ft. Total Length of Pump
 ft. in. drop pipe & No. Cable
 ft. in. air line
 in. Pit. ft. bury in outlet

WELL MATERIALS

103 ' of 24 " diameter of Outer Casing
52 ' of 23 " diameter of Open Hole
322 ' of 20 " diameter of Inner Casing
156 ' of 19 " diameter of Open Hole
312 ' of 16 " liner from 312 to 354
354 ' to 0 Mix grout 270 (Sacks)
" diameter Screen

RECORD OF TEST PUMPING

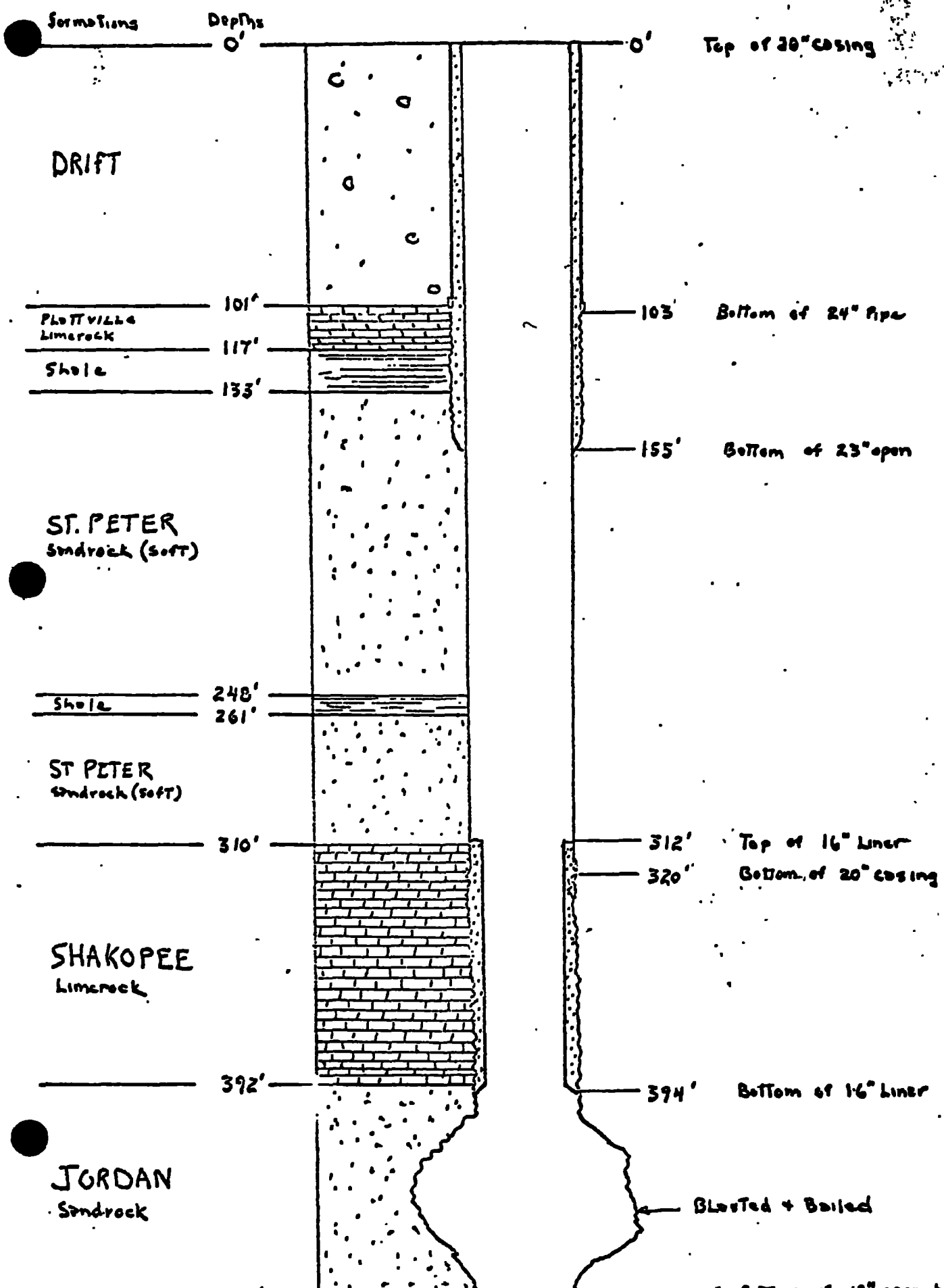
Static Water Level ft. from
100 GPM D.D. Hours
353 GPM 48' 8" D.D. 2 Hours
473 GPM 54' 9" D.D. 5 1/2 Hours
633 GPM 69' 8" D.D. 2 Hours
 GPM D.D. 1 1/2 Hours

Remarks: After its 1st test - 16" liner
was installed from 312' to 354' which
put off the Shakopee formation
and then the well is being blasted
and bailed in the 1st part of the
Jordan formation

WELL LOG - INNERTONKA VILLAGE WELL #6

ENGINEER - Schoell & Madson

CONTRACTOR - KERS Well Drilling Co.



WELL RECORD

KEYS WELL DRILLING COMPANY

WATER PRODUCERS

SAINT PAUL, MINNESOTA

Owner VILLAGE OF MINNETONKADate Completed Partial 5/2/67Location Co. Rd. #73 & Cedar Lake RoadDriller Floyd D'ArienWell No. 7Size 24 x 20Total Depth 334(?)Type 2

DRILLERS LOG

0 to 104 Drift
104 to 112 Shale
112 to 121 Limerock
121 to 135 Shale
135 to 249 Sandrock (soft)
249 to 261 Shale
261 to 304 Sandrock
304 to 315 Shakopco (broken)
315 to 339 Shakopco (sandy)
 to
 to
 to
 to
 to

PERMANENT PUMP DATA

Mfg. Type Serial No.
Capacity GPM TDH
Motor Make Type
H. P. Volts Ph. RPM
 ft. in. Col. pipe in. Shaft
 ft. in. Bowls Stages Type
 ft. in. suction pipe &
 ft. Total Length of Pump
 ft. in. drop pipe & No. Cable
 ft. in. air line
 in. F-less ft. bury in. outlet

WELL MATERIALS

114 of 24 " diameter of Outer Casing
38 of 23 " diameter of Open Hole
315 of 20 " diameter of Inner Casing
24 of 20 " diameter of Open Hole
 to Mix grout (yds.) (Sacks)
 " diameter Screen

RECORD OF TEST PUMPING

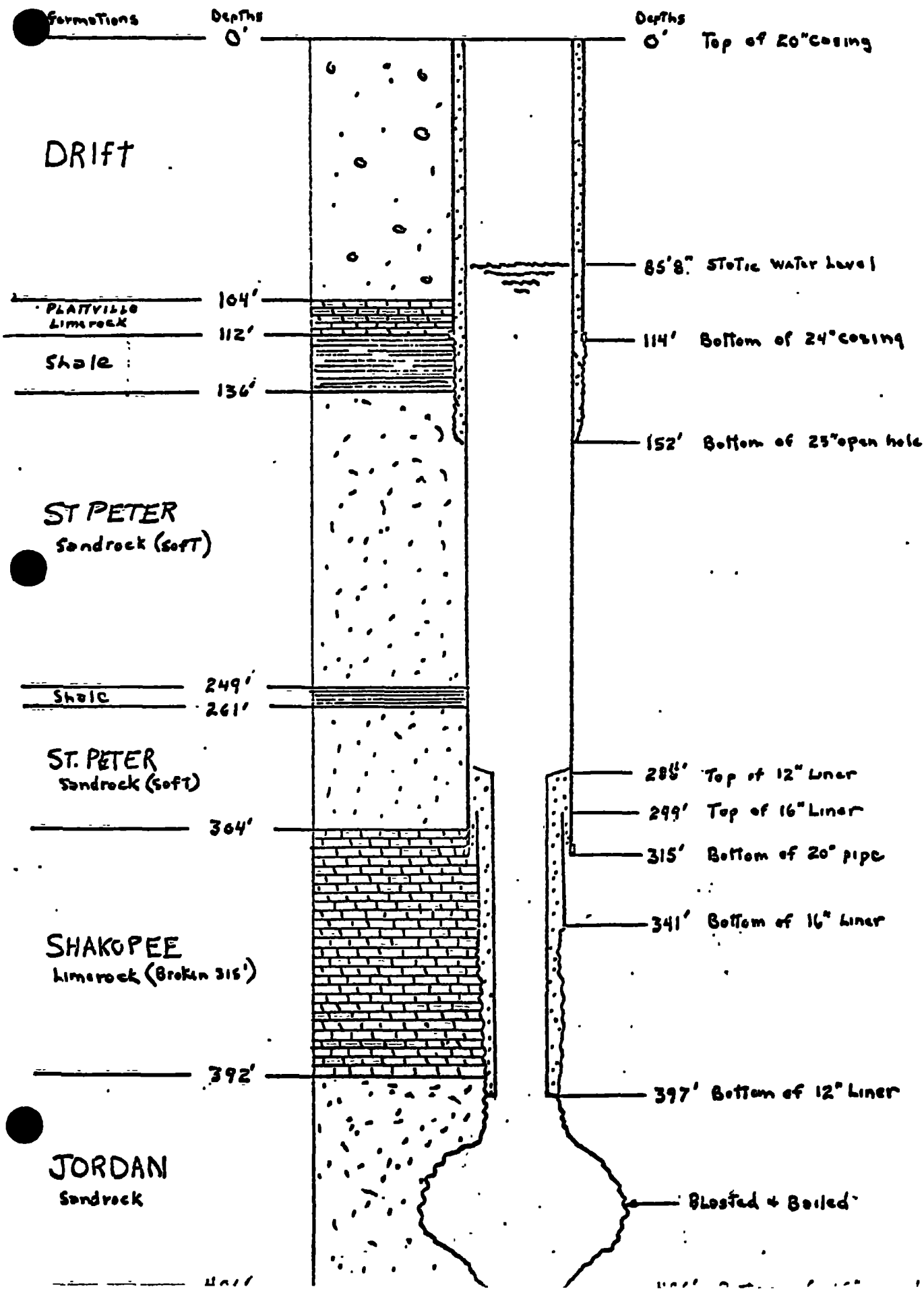
Static Water Level ft. from
 GPM D.D. Hours
 GPM D.D. Hours
 GPM D.D. Hours
 GPM D.D. Hours
 GPM D.D. Hours

Remarks: Drilling was stopped at 339'
because of sandrock running into
hole. Hole was bailed to 322' and filled
with 70 sacks of concrete and then
drilled out and when we reached 339'
again it again filled back up to 325'

WELL LOG , INNENETONKA VILLAGE WELL #7

ENGINEER - Schoell + Madson

CONTRACTOR - KEYS Well Drilling Co.



REPORT

Tack No. _____

Well No. _____

223938

Town Minneapolis

Date Started _____

Machine No. _____ State Minnesota

Owner American Hardware Mutual Ins.

Total Depth of Well 520'

NON-RESPONSIVE

DIAMETER OF HOLE	16"	12"	10"	PA
Top of Pipe above Surface	16'	92'	16'	75-616'
Bottom of Pipe below Surface	102'9"	204'	284'	
No. of Ft. of Pipe in the Hole	85'9"	112'	268'	
No. of Ft. of Hole Drilled				

TEST	1	2	3	4	FORMATION	Thickness	Depth
Depth of the Hole	520				Sand & Gravel	18	0-18
Depth to Water at Rest	60				Sand & Gravel	15	8-33
Depth to Water Pumping	66				Sand (wet)	14	17-47
Depth of Pump Pipe	700				Blue Clay	6	47-53
Gallons per minute	Yes				Water Sand	43	53-96
Will well supply more?	Yes				Sand & Gravel - Broken	19	96-115
Was Strainer in Hole?	Yes				Sand & Gravel	13	115-128
Was water clear?	Yes				Sand & Gravel	47	128-175
Was well pumping sand?					Gravel - S of Sandrock	20	175-195
Hours Pumping					Yellow Shale & Sandrock	15	195-210
					Sandrock & Shale	60	210-270
					Limestone	20	270-291
					Sandrock	129	291-520

STRAINER

Make _____

Type of Metal _____

Diameter O. D. _____

Diameter I. D. _____

Total Length _____

Number _____

Top of Screen below Surface _____

No. of Ft. Exposed _____

Bottom of Screen below Surface _____

Was Str. wired _____

Did Sand come thru Str. _____

Was Str. coarse enough _____

Style of Fittings _____

All measurements taken from Drilling

Drilling Platform 18' above boiler room floor.

885
195
690 - T/OSTP

270
195 - T/OPDC

391
494 - T/CJDN

LOCATED BY

- ☐ Address Verification
- ☐ Name on Mailbox
- ☐ Lot-Block
- ☐ Plat Book
- ☐ Info. From Owner
- ☐ Info. From Neighbor
- ☒ Other Survey not
- ☐ Can't Locate State Why

9630359

QUALITY ASSURANCE PROJECT PLAN

Page: 1 of 125

Date: Jan. 1987

Number: QA E415

Revision: 0

**QUALITY ASSURANCE PROJECT PLAN
FOR SAMPLING AND ANALYSIS - GROUNDWATER
AND GAC PLANT MONITORING**

**Prepared for
The City of St. Louis Park
St. Louis Park, MN 55416**

**ERT - A RESOURCE ENGINEERING COMPANY
696 Virginia Road, Concord, Massachusetts 01742**

0053F PE-415

TABLE OF CONTENTS

1.	TITLE PAGE	1
2.	TABLE OF CONTENTS	2
3.	PROJECT DESCRIPTION	7
3.1	Background	7
3.2	Objectives	8
4.	PROJECT ORGANIZATION AND RESPONSIBILITY	10
5.	QUALITY ASSURANCE OBJECTIVES	13
6.	SAMPLING PROCEDURES	15
6.1	Training	15
6.2	Document Control	15
6.3	Sample Control Procedures and Chain of Custody	25
6.3.1	Sample Identification	25
6.3.2	Chain-of-Custody Procedures	28
6.3.3	Field Forms	30
6.4	Sampling Procedures - GAC Plant	31
6.5	Groundwater Sampling and Water Level Measurements	33
6.5.1	Decontamination	33
6.5.2	Field Blanks	33
6.5.3	Sample Containers	34
6.5.4	Sample Collection - Monitoring Wells	36
6.5.5	Sample Collection - Piezometers	36
6.5.6	Sample Collection - Municipal Pumping Wells	36
6.6	Sample Preservation, Shipment and Storage	37
6.7	Field Measurement Equipment	37
6.8	Duplicate Samples	37
7.	SAMPLE CUSTODY	39
7.1	Chain of Custody	39
7.2	Record Keeping	39
7.3	Final Evidence Files	47

TABLE OF CONTENTS (Continued)

8.	CALIBRATION PROCEDURES	50
8.1	Low Level (ppt) Analysis of PAH and Heterocycles	50
8.1.1	Daily GC/MS Performance Tests	50
8.1.2	Gas Chromatography/Mass Spectrometry Analysis	55
8.2	Extended Analyses Calibration	58
8.2.1	Daily GC/MS Performance Tests	60
8.2.2	Gas Chromatography/Mass Spectrometry Analysis	60
8.3	Calibration for Phenolics	61
8.4	Calibration for Expanded Analyses	63
8.5	Non-criteria PAH Analysis Calibration	63
9.	ANALYTICAL PROCEDURES	68
9.1	Low Level (ppt) Analysis of PAH and Heterocycles	68
9.1.1	Summary	68
9.1.2	Interferences	68
9.1.3	Apparatus	68
9.1.4	Extraction	73
9.1.5	GC/MS Calibration	74
9.1.6	Daily GC/MS Performance Tests	75
9.1.7	Gas Chromatography/Mass Spectrometry Analysis	75
9.1.8	Calculations	78
9.2	Extended Analyses for Carcinogenic PAH in GAC Plant	81
9.3	Extended Analyses for Phenolics in GAC Plant	81
9.4	Expanded Analyses	81
9.5	Non-Criteria PAH Analyses	84
10.	DATA REDUCTION, VALIDATION AND REPORTING	88
10.1	Data Reduction and Validation	88

TABLE OF CONTENTS (Continued)

10.2 Turnaround Time	88
10.3 Report Descriptions	88
10.3.1 Method Detection Limit Report	88
10.3.2 Sampling Report	90
10.3.3 Analytical Results Report	90
10.3.4 Surrogate Recovery Report	92
10.3.5 Matrix Spike Recovery Report	92
10.3.6 Reporting Requirements for Samples Exceeding Advisory Levels or Drinking Water Criterion	92
11. INTERNAL QUALITY CONTROL CHECKS	97
11.1 Low Level PAH Analysis/Extended Analyses	
Non-criteria PAH Analyses	97
11.1.1 Method Detection Limit	97
11.1.2 Method Blank and Solvent Blank	97
11.1.3 Surrogates	99
11.1.4 Matrix Spikes	100
11.1.5 Duplicates	101
11.2 Extended Analyses for Phenolics	101
11.3 Expanded Analyses	103
12. PERFORMANCE AND SYSTEM AUDITS	105
12.1 Interlaboratory Performance Surveys	105
12.2 Periodic In-House Audits	106
12.2.1 Performance Audits	106
12.2.2 Systems Audits	108
13. PREVENTIVE MAINTENANCE	110
13.1 Service Contracts	110
13.2 Instrument Logbooks	110

TABLE OF CONTENTS (Continued)

14. SPECIFIC PROCEDURES TO ASSESS DATA PRECISION	
ACCURACY AND COMPLETENESS	111
14.1 External and Internal Components	111
14.1.1 External Components: Accuracy and Precision Measurements	111
14.1.2 Internal Components: Accuracy and Precision Measurements	112
14.2 Control Charts	113
14.2.1 Accuracy	113
14.2.2 Precision	113
14.2.3 Limits	113
14.3 Suspicious/Out-of-Control Events	113
14.3.1 Outliers	114
14.3.2 Runs	114
14.3.3 Trends	114
14.3.4 Periodicity	114
14.4 Completeness	114
15. CORRECTIVE ACTION	115
15.1 Low Level PAH Analyses/Extended Analyses/Non-criteria PAH Analyses	115
15.1.1 Surrogates	115
15.1.2 Matrix Spikes	117
15.2 Extended Analysis for Phenolics	117
15.2.1 Surrogates	117
15.2.2 Matrix Spikes	118
15.3 Expanded Analyses	118
15.3.1 Volatile Organics	118
15.3.2 Acid, Base/Neutral Extractable Organics	121

QUALITY ASSURANCE PROJECT PLAN

Page: 6 of 125
Date: Jan. 1987
Number: QA E415
Revision: 0

TABLE OF CONTENTS (Continued)

15.3.3 Priority Pollutant Metals	122
15.3.4 Other Inorganic	122
15.4 Other Corrective Actions	123
15.4.1 Samples	123
15.4.2 Sample Extracts	123
15.4.3 Quality Control Samples	123
15.4.4 Performance and System Audits	124
16. QUALITY ASSURANCE REPORTS TO MANAGEMENT	125
16.1 Performance and System Audits	125
APPENDIX A	STANDARD OPERATING PROCEDURES
APPENDIX B	ANALYTICAL METHODS
APPENDIX C	HISTORY OF RESPONSE ACTIONS

3. PROJECT DESCRIPTION

3.1 Background

Groundwater in the city of St. Louis Park, Minnesota has been contaminated by activities at a coal-tar distillation and wood preserving plant operated from 1917 to 1972. Numerous previous studies have identified polynuclear aromatic hydrocarbons (PAH) present in various aquifers beneath St. Louis Park and adjacent communities.

The United States Environmental Protection Agency (EPA), the Minnesota Pollution Control Authority (MPCA), the Minnesota Department of Health (MDH), the City of St. Louis park (SLP), and Reilly Tar & Chemical Corporation (Reilly) have agreed to acceptable water quality criteria for PAH. These criteria, as incorporated into the Consent Decree, include the following concentration levels:

	<u>Advisory Level</u>	<u>Drinking Water Criteria</u>
• Sum of benzo(a) pyrene and dibenz(a,h) anthracene	3.0 ng/l*	5.6 ng/l
• Carcinogenic PAH	15 ng/l	28 ng/l
• Other PAH	175 ng/l	280 ng/l

*or the lowest concentration that can be quantified,
whichever is greater

In conjunction with the implementation of remedial measures to limit the spread of contaminants, a granular activated carbon (GAC) treatment system has been installed to treat water from St. Louis Park (SLP) wells 10 and 15. Further provisions of the Remedial Action Plan (RAP) call for long-term monitoring of the influent and effluent of the GAC treatment plant and the major aquifers underlying the region. The general objective of the monitoring program is to identify the distribution of PAH and/or phenolics in the ground water. The analytical data will be used to evaluate contamination by comparing the levels of PAH and/or phenolics found in the various samples with historical water quality data and with water quality criteria established in the consent Decree-RAP. The specific objectives of the sampling and analysis program, and therefore, the intended end use of the data vary slightly for the different aquifers being monitored in accordance with the Consent Decree-RAP.

3.2 Objectives

The GAC plant monitoring is being done to assess and continuously evaluate the performance of the treatment system. Analytical results for influent and effluent samples will be compared to the drinking water criteria for PAH as established in the Consent Decree-RAP. Based on these comparisons, decisions will be made on: 1) possible modifications to the treatment system (e.g., adding another carbon column), 2) system operations (e.g., when the carbons should be replaced), and 3) cessation of the treatment system, if desired, when sufficiently low concentrations of PAH in influent samples are demonstrated.

The objective of sampling the four existing Mt. Simon-Hinckley Aquifer municipal drinking water wells, and sampling any new Mt. Simon-Hinckley Aquifer municipal drinking water wells installed within one mile of well W23, and analyzing for PAH is to assure the continued protection of these wells from PAH resulting from activities of Reilly at the site. The analytical data will be used to make comparisons between the levels of PAH found in the Mt. Simon-Hinckley Aquifer, and the drinking water criteria established in the Consent Decree-RAP.

The objective of sampling and analyzing the Ironton-Galesville Aquifer source control well (W105) is to assess the levels of PAH in the discharge from W105 when it is pumping a monthly average of 25 gallons per minute. The data will be used to compare the concentration of total PAH in the samples to a cessation criterion of 10 micrograms per liter of total PAH established in the Consent Decree-RAP. Also, if any new Ironton-Galesville Aquifer drinking water wells are installed within one mile of well W23, then those wells will be sampled and analyzed for PAH to meet the objective of assuring protection of the well from PAH resulting from the activities of Reilly at the site. The analytical data would be used to compare the levels of PAH found in potential Ironton-Galesville Aquifer drinking water wells to the drinking water criteria established in the Consent Decree-RAP.

The objectives of monitoring the many Prairie du Chien-Jordan Aquifer wells, including municipal drinking water wells, private or industrial wells, and monitoring wells are to: 1) monitor the distribution of PAH in the aquifer, thus evaluating the source and gradient control system, and 2) assure the continued protection of drinking-water wells from PAH resulting from the activities of Reilly at the site. The analytical data will be used to compare the levels of PAH in the Prairie du Chien-Jordan aquifer to historical PAH data and to various criteria established in the Consent Decree-RAP (e.g., drinking water criteria for drinking water wells, and a cessation criterion of 10 micrograms per liter of total PAH for source control well W23). Analytical data for samples of the discharge from gradient control well SLP4 will be compared to discharge limitations in and NPDES permit which will be applied for at the conclusion of a Feasibility Study to determine the appropriate disposition of SLP4 discharge. Water

level data will be used to evaluate ground-water flow patterns in the Prairie du Chien-Jordan Aquifer.

The objective of monitoring St. Peter Aquifer wells is to determine the nature and extent of PAH in the St. Peter Aquifer resulting from the activities of Reilly at the site. The analytical data will be used to compare the levels of PAH in the St. Peter Aquifer to historical PAH data and to the drinking water criteria established in the Consent Decree-RAP. Water level data will be used to evaluate ground-water flow patterns in the St. Peter Aquifer.

The objectives of monitoring the Drift-Platteville Aquifer wells are to: (1) monitor the distribution of PAH and phenolics in the aquifer, thus evaluating the source and gradient control systems, and (2) to further define the nature and extent of PAH and phenolics in the Northern Area of the Drift-Platteville Aquifer resulting from the activities of Reilly at the site. The analytical data will be used to compare levels of PAH and phenolics in the Drift-Platteville Aquifer with historical water quality data for the aquifer and with various criteria established in the Consent Decree-RAP for PAH and phenolics. Water level data will be used to evaluate ground-water flow patterns in the Drift-Platteville Aquifer.

This Site Management Plan outlines the scope of work to be performed in order to monitor the ground water in the St. Louis Park, MN area in accordance with the Consent Decree-RAP related to the Reilly Tar & Chemical Corp. N.P.L. site. Included in this plan are: (1) the identity of wells to be monitored, (2) the schedule for ground-water monitoring, and (3) a description of the procedures that will be used for sample collection, water level measurement, sample handling, sample analysis, and reporting.

The time period covered by the Initial Sampling Plan is from the date of its acceptance and approval by the agencies, to December 31, 1987. This is one year longer than the initial Plan is required to cover as stated in the RAP (Section 3). The reason for this change is that, according to the schedule in the RAP, a Sampling Plan for 1987 would be due before comments were received on the Initial Sampling Plan. Therefore, to avoid that situation, and to present a clear picture of ground-water monitoring activities through the first year of monitoring, this Plan covers sampling through the 1987 calendar year. The first subsequent Sampling Plan (RAP Section 3.3) will be submitted by October 31, 1987, covering the 1988 calendar year.

This Plan incorporates the requirements of RAP Sections 3.2, 3.3, 4.3, 5.1, 6.1.4, 7.3, 8.1.3, 9.1.3, 9.2.3, 9.3.3, and 9.6. Some of the sampling required under RAP Section 4.3 (Monitoring the GAC System) has already taken place prior to the Effective Date. Therefore, only the monitoring that will take place from the approval date of this Initial Sampling Plan through December 31, 1987 is included in this Plan.

4. PROJECT ORGANIZATION AND RESPONSIBILITIES

This project is being conducted in accordance with the Consent Decree Remedial Action Plan for the Reilly Tar & Chemical Corporation N.P.L site in St. Louis Park, Minnesota. The parties to the Consent Decree include Reilly, the City of St. Louis Park, U.S. EPA, MPCA, and MDH. The project organization shown in Figure 4-1 indicates the involvement of the parties to the Consent Decree, as appropriate. The Laboratory Quality Control Coordinator is appointed by the Chemistry Division Quality Control Manager, who reports directly to the Division Director, with ancillary responsibilities to the Laboratory Manager and the Corporate Quality Assurance Manager. All other functions in the organizational structure report directly through line management. Responsibilities of the key positions in the organization are described below:

- Project Manager: The Project Managers' responsibilities include scheduling of activities, project communication, and general overview of the program progress.
- Laboratory Manager: The Laboratory Manager is responsible for overall management of laboratory operations to meet project commitments, including scheduling of personnel and physical resources.
- Quality Assurance Officer: The Quality Assurance Officer is responsible for overall quality control oversight. His duties will include performance and system audits and supervision of activities of the Project QC Officer.
- Laboratory QC Coordinator: The Laboratory QC Coordinator is responsible for maintaining the laboratory Quality Control program. The Laboratory QC Coordinator maintains laboratory standards and traceability documentation and performs analytical data package validation. The Laboratory QC Coordinator reports directly to the Laboratory Manager, but also has indirect reporting responsibility to the Quality Assurance Manager.
- Field Coordinator: The Field Coordinator is responsible for the coordination and effective use of all personnel on site and for maintaining a record of field activities. The Field Coordinator will also be responsible for field quality control including issuance and tracking of measurement and test equipment, the proper labeling, handling, storage, shipping, and chain of custody procedures used at the time of sampling, and control and archiving of all field documentation, (log books, notebooks, data sheets, etc.) generated during the field investigation.
- Sampling Personnel: The Sampling Personnel responsibilities include collecting samples; conducting field measurements (e.g. water level); and maintaining proper decontamination procedures;

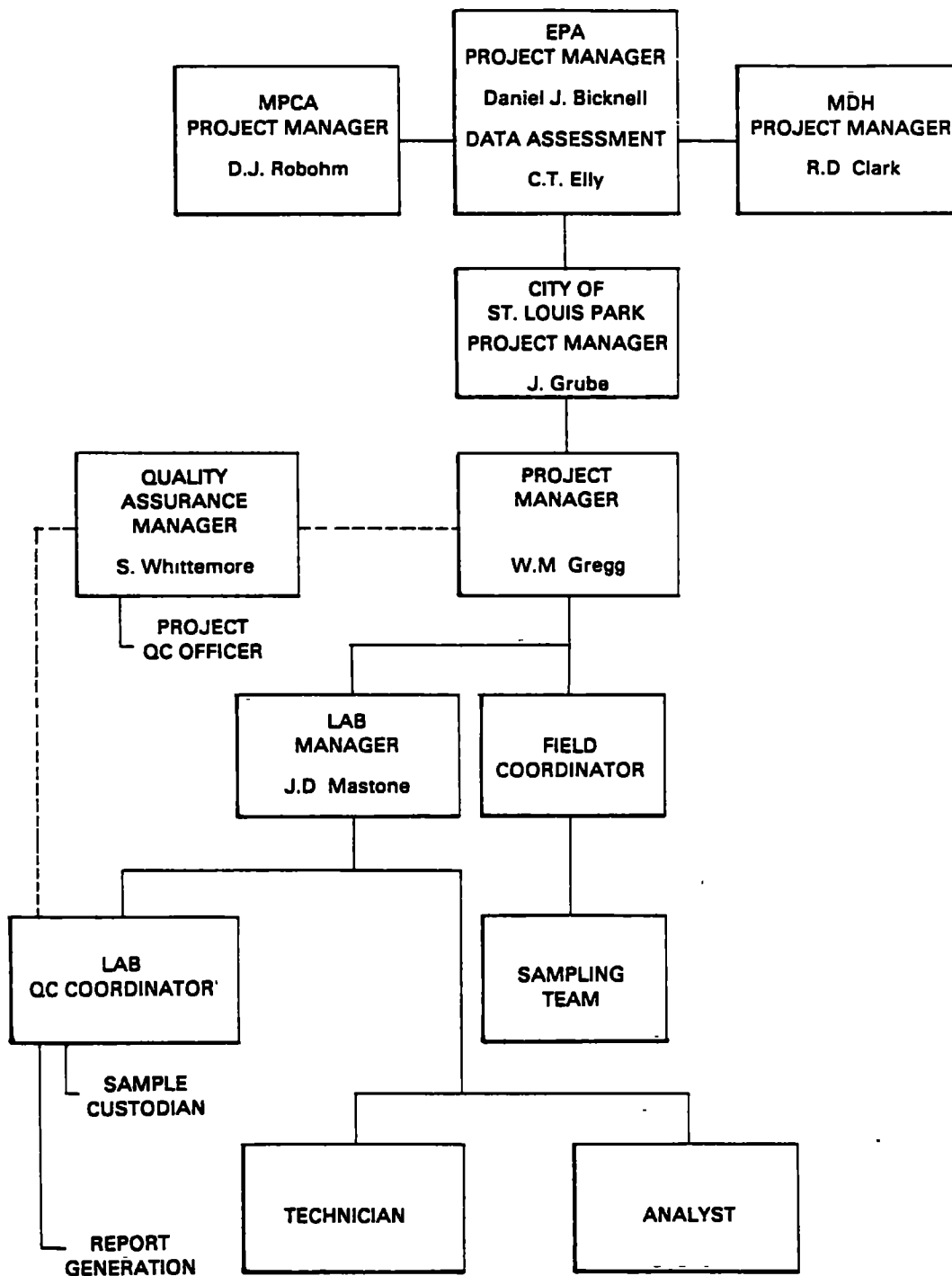
QUALITY ASSURANCE PROJECT PLAN

Page: 11 of 125

Date: Jan. 1987

Number: QA E415

Revision: 0



8701021

Figure 4-1 Project Organizational Chart

all according to documented procedures stated in the Quality Assurance Project Plan and the corresponding SOPs.

- Analyst: The Analyst is responsible for the analysis of water samples for the requested parameters utilizing the methods prescribed by this plan.
- Technician: The Technician is responsible for sample extraction (according to documented procedures). This requires practical experience and knowledge in the techniques of liquid- liquid solvent extraction, Kuderna Danish evaporation, and the quantitative preparation of sample extracts for analysis.

5. QUALITY ASSURANCE OBJECTIVES

The principal objectives of this plan pertain to the collection of data that are sufficient to monitor the effectiveness of the GAC treatment system and to detect changes in groundwater quality. Therefore, the quality of the data gathered in this project can be defined in terms of the following elements:

- **Completeness** - a sufficient number of successful (valid) measurements to characterize the concentrations of PAH in the influent and effluent of the treatment system and in the aquifers of interest over a period of time.
- **Representativeness** - the extent to which reported analytical results truly depict the PAH concentrations in the sampled environment. Representativeness is optimized through proper selection of sampling sites, times and procedures, through proper sample preservation, and through prompt extraction and analysis.
- **Accuracy and Precision** - Accurate and precise data will be achieved through the use of sampling and analytical procedures that minimize biases, through the use of standard procedures, through the meticulous calibration of analytical equipment and by implementing corrective action whenever measured accuracy and precision exceed pre-established limits. Accuracy and precision will be measured by the analysis of method spikes and duplicate samples.
- **Sensitivity** - determination of instrument sensitivity is accomplished by calibration using multiple concentrations of the analytes of interest. Once instrument sensitivity is demonstrated, analysis of replicate spiked samples of deionized reagent water at a concentration of 1-5 times the instrument sensitivity, is used to determine method sensitivity (i.e. method detection limit)
- **Comparability** - the extent to which comparisons among separate measurements will yield valid conclusions. Comparability among measurements in the SLP monitoring program will be achieved through the use of rigorous standard sampling and analytical procedures.
- **Traceability** - the extent to which results can be substantiated by hard-copy documentation. Traceability documentation exists in two forms: that which links final numerical results to authoritative measurement standards, and that which explicitly describes the history of each sample from collection to analysis.

The fundamental mechanisms that will be employed to achieve these quality goals can be categorized as prevention, assessment and correction, as follows:

- 1) Prevention of defects in the quality through planning and design, documented instructions and procedures, and careful selection and training of skilled, qualified personnel;
- 2) Quality assessment through a program of regular audits and inspections to supplement continual informal review;
- 3) Permanent correction of conditions adverse to quality through a closed-loop corrective action system.

The St. Louis Park sampling program Quality Assurance Project Plan has been prepared in direct response to these goals. This plan describes the quality assurance program to be implemented and the quality control procedures to be followed by ERT during the course of the site investigation studies for the St. Louis Park (SLP) site. The QA objectives will include field blanks, method blanks, field duplicates, surrogate spikes, and matrix spikes. Precision, accuracy and completeness criteria are established for each parameter of interest. The specific criteria for each analysis and parameter are set forth in detail in the following sections:

<u>Objective</u>	<u>Frequency</u>	<u>Sections Discussing Criteria</u>
Field Duplicates	10%	6.8, 11.1.5
Field Blanks	10%	6.5.2
Method Blanks	10%	11.1.2
Surrogate Spikes	100% of GC/MS analyses	11.1.3, 15
Matrix Spikes	5%	11.1.4, 15

6. SAMPLING PROCEDURES

Samples will be collected by ERT and SLP personnel. The overall sampling program is summarized in Tables 6-1 and 6-2, and Figures 6-1 through 6-5. This section discusses general QAPP provisions relevant to sample collection, containerization, packaging and shipping activities.

6.1 Training

All ERT and SLP personnel working on the project will be properly trained, qualified individuals. Prior to commencement of work, personnel will be given instruction specific to this project, covering the following areas:

- Organization and lines of communication and authority
- Overview of the Site Management Plan and QA Project Plan,
- Documentation requirements,
- Decontamination requirements,
- Health and Safety considerations.

Training of field personnel will be provided by the Field Coordinator or his/her qualified designee.

The analysts performing chemical analyses of samples will be trained in and will have exhibited proficiency in the analytical methods to be employed.

6.2 Document Control

Document Control for the Initial Sampling Plan serves a two-fold purpose. It is a formal system of activities that ensures that:

- 1) All participants in the project are promptly informed of revisions of the Quality Assurance Project Plan; and
- 2) All documents generated during the course of the program are accounted for during, and at the end of the project.

This QA Project Plan and all Standard Operating Procedure documents have the following information on each page:

TABLE 6-1 INITIAL SAMPLING PLAN GAC PLANT
MONITORING SCHEDULE ^(a)

<u>RAP Section</u>	<u>Sampling Points</u>	<u>Start of Monitoring</u>	<u>Sampling Frequency</u>	<u>Analyses</u> ^(b)
4.3.1 (C)	Treated water(TRTD)	Date of plan approval	Monthly	PAH(ppt) ^(c)
4.3.3 (C)	Feed water(FEED)	Date of plan approval	Quarterly	PAH(ppt)
4.3.4	Treated water	Date of plan approval	Annually	Extended PAH(ppt)
4.3.4	Treated or Feed water	Date of plan approval	Annually	Acid fraction compounds in EPA Test Method 625.

- (a) This schedule does not include certain contingencies (eg. exceedance monitoring) and, therefore, represents the minimum program that is likely to occur between the date this Plan is approved and December 31, 1987. Sections 4 and 12 of the RAP outline the additional sampling that will be conducted if PAH criteria are exceeded. The first samples will be collected during the period indicated by the monitoring frequency following the date of the start of monitoring. The location of the GAC plant is shown in Figure 6-1.
- (b) Lists of parameters and methods for analysis of PAH, extended PAH, and acid fraction compounds in EPA Test Method 625 are provided in the QAPP. Field blanks will be collected and analyzed at a frequency of one per day. Duplicate samples will be collected and analyzed at a frequency of one per 10 samples.
- (c) ppt = parts per trillion. This signifies analysis using selected ion monitoring gas chromatography mass spectrometry.

TABLE 6-2 INITIAL SAMPLING PLAN GROUND-WATER MONITORING SCHEDULE ^(a)

<u>Source of Water</u>	<u>RAP Section</u>	<u>Sampling^(l) Points</u>	<u>Start of Monitoring</u>	<u>Sampling Frequency</u>	<u>Analyses^(b)</u>
Mt. Simon-Hinckley Aquifer	5.1	SLP11, SLP12, SLP13, SLP17	Within six months of Effective date ^(g)	Annually	PAH (ppt) ^(c)
	5.3.2	New municipal wells within one mile of well W23	At the time of installation	Annually	PAH(ppt)
Ironton-Galesville Aquifer	6.1.4	W105 W38 ^(e)	Start of pumping	Quarterly	PAH (ppb) ^(d)
	6.2.1	New municipal wells within one mile of well W23	At the time of installation	Annually	PAH(ppt)
Prairie du Chien-Jordan Aquifer	7.3 (A)	SLP4	Start of pumping	Quarterly	PAH (ppt) ^(h) phenolics
	7.3 (B)	W23	Start of pumping	Quarterly	PAH (ppb)
	7.3 (C)	SLP6, SLP7 or SLP9, W48	Date of plan approval	Quarterly	PAH (ppt)
	7.3 (D) ^(m)	AHM or MGC ⁽ⁱ⁾ , E2, E13, H3, SLP10 or SLP15, SLP14, SLP16, W402 ^(j) W403, W119	Date of plan approval	Semi-annually	PAH (ppt)
	7.3 (E) ^(m)	SLP5, H6, E3, E15, MTK6, W29, W40, W70, W401 ^(j)	Date of plan approval	Annually	PAH (ppt)
	7.3 (F)	W112, W32, SLP8, SLP10, E4, E7	Date of plan approval	Quarterly	No chemical analyses ^(f)
St. Peter Aquifer	8.1.3	SLP3, W14, W24, W33, W122, W129 W133, P116, plus 5 new wells	Within 30 days of installing new wells	Once	PAH (ppt)
		SLP3 plus six of the wells listed above ⁽ⁿ⁾	Within 6 months of above	Once	PAH (ppt)

TABLE 6-2 (continued)

<u>Source of Water</u>	<u>RAP Section</u>	<u>Sampling^(l) Points</u>	<u>Start of Monitoring</u>	<u>Monitoring Frequency</u>	<u>Analyses^(b)</u>
Drift-Platteville Aquifer	9.1.3 and 9.2.3	Source and gradient control wells (3 wells)	Start of pumping	Quarterly	PAH (ppb) and total phenols
	9.3.3	W131, W136, plus 6 new wells	Within 30 days of well installations	Once	Expanded analysis
	9.3.3	W131, W136 plus 6 new wells	Within 6 months of above	Once	PAH(ppb) and total phenols
	9.6	Drift: W2, W5, W15, W11, W12, W16, W116, W117, W128, W135, W136, PB140; Platteville: W1, W19, W20, W22, W115, W120, W121, W123, W130, W131, W132, W143, plus 6 new wells	Concurrent ^(k) with 9.3.3 sampling	Concurrent ^(k) with 9.3.3 sampling	PAH (ppb) and total phenols

- (a) This schedule does not include certain contingencies (eg. exceedance monitoring) and, therefore, represents the minimum program that is likely to occur between the date this Plan is approved and December 31, 1987. Section 12 of the RAP outlines the additional sampling that will be conducted if the drinking water criteria are exceeded in samples from water supply wells. The first samples will be collected during the period indicated by the monitoring frequency following the date of the start of monitoring. Field blanks will be collected at a frequency of one per day, and one duplicate sample will be collected for every 10 samples.
- (b) Lists of parameters and descriptions of the methods for analysis of PAH, phenolics, and expanded analyses are provided in the QAPP. Water levels will be measured each time samples are collected for analysis, except for those wells which prove to be inaccessible for such measurements.
- (c) ppt = parts per trillion. This signifies analysis using selected ion monitoring gas chromatography mass spectrometry.
- (d) ppb = parts per billion. This signifies analysis by EPA Method 625. If analytical results for individual wells are below 20 micrograms per liter (20 ppb) using this method, then the part per trillion method will be used on subsequent monitoring rounds.
- (e) Water levels in W38 will be measured each time W105 is sampled.
- (f) Water levels only (no monitoring) will be measured at these wells, except for those wells which prove to be inaccessible for such measurements.

TABLE 6-2 (continued)

- (g) Or within 30 days of the approval date of this Plan, whichever is later.
- (h) SLP4 analytical program will be determined by the results of the Feasibility Study.
- (i) AHM = American Hardware Mutual, MGC = Minikahda Golf Course.
- (j) Wells W401, W402, and W403 may or may not be available for sampling at the same time as the other wells on these lists. They will be sampled in conjunction with the monitoring performed in accordance with the schedule shown, once they are available for sampling.
- (k) If the six new Drift-Platteville Aquifer monitoring wells have not been installed by the appropriate time, then monitoring of the wells listed here will be done semi-annually for the first year following the effective date. There will be other opportunities for concurrent sampling. If the six new Drift-Platteville Aquifer monitoring wells are available for concurrent sampling, then the following eight wells will be omitted from the first sampling round, due to the Regional Administrator and Director's request for the eight expanded analysis as shown for RAP Section 9.3.3: W1, W2, W22, W116, W123, W128, W130, and PB140.

If any of the wells listed here become damaged, destroyed, or otherwise unsuitable for sampling, alternate wells will be selected by the Project Leaders for monitoring.
- (l) Sampling points are located on the maps shown in Figures 6-1 through 6-5. Letter prefixes to well codes are defined as follows:
 - W - 4-inch monitoring well
 - P - monitoring piezometer
 - PB - 2-inch monitoring well
 - SLP - St. Louis Park supply well
 - E - Edina supply well
 - H - Hopkins supply well
 - MTK - Minnetonka supply well
- (m) Water level measurements will be made quarterly at these wells, except for those wells which prove to be inaccessible for such measurements.
- (n) The six St. Peter Aquifer monitoring wells that will be monitored according to RAP Section 8.1.3 will be selected by the Project Leaders based on the results of the first monitoring round.

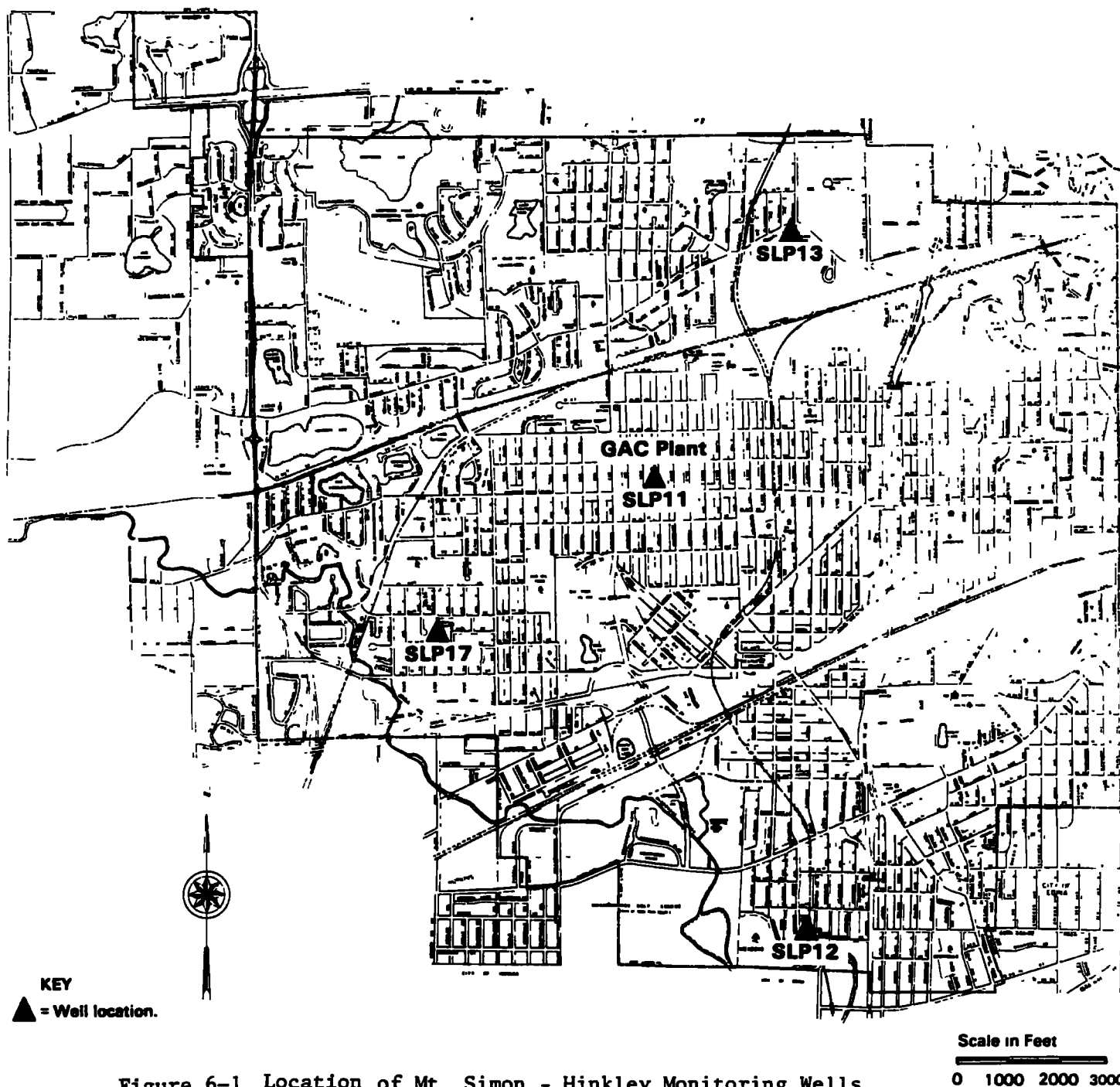


Figure 6-1 Location of Mt. Simon - Hinkley Monitoring Wells and St. Louis Park GAC Water-treatment Plant

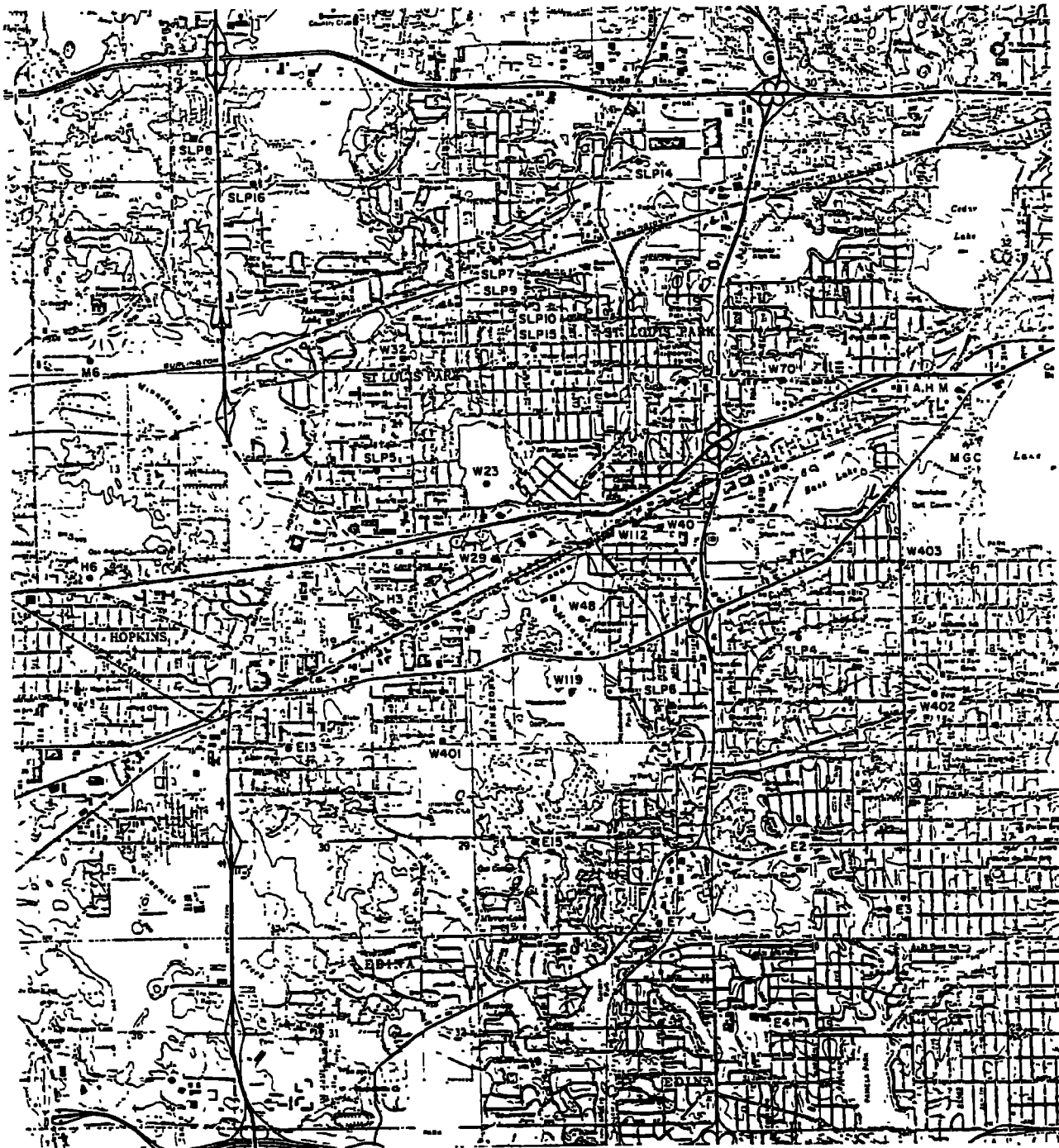


Figure 6-2 Location of Praire du Chien-Jordan Aquifer Wells

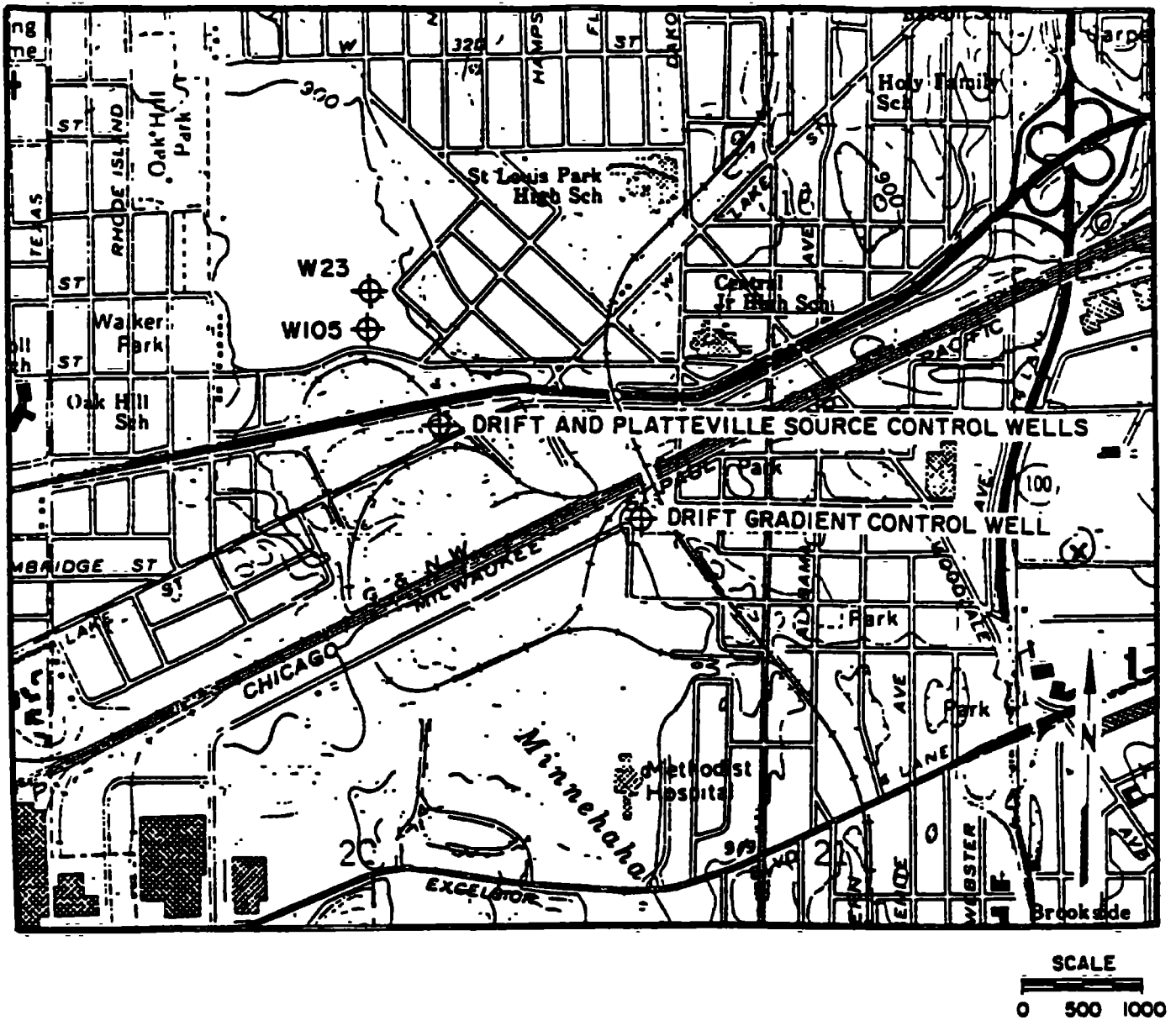


Figure 6-3 Location of Source and Gradient Control Wells

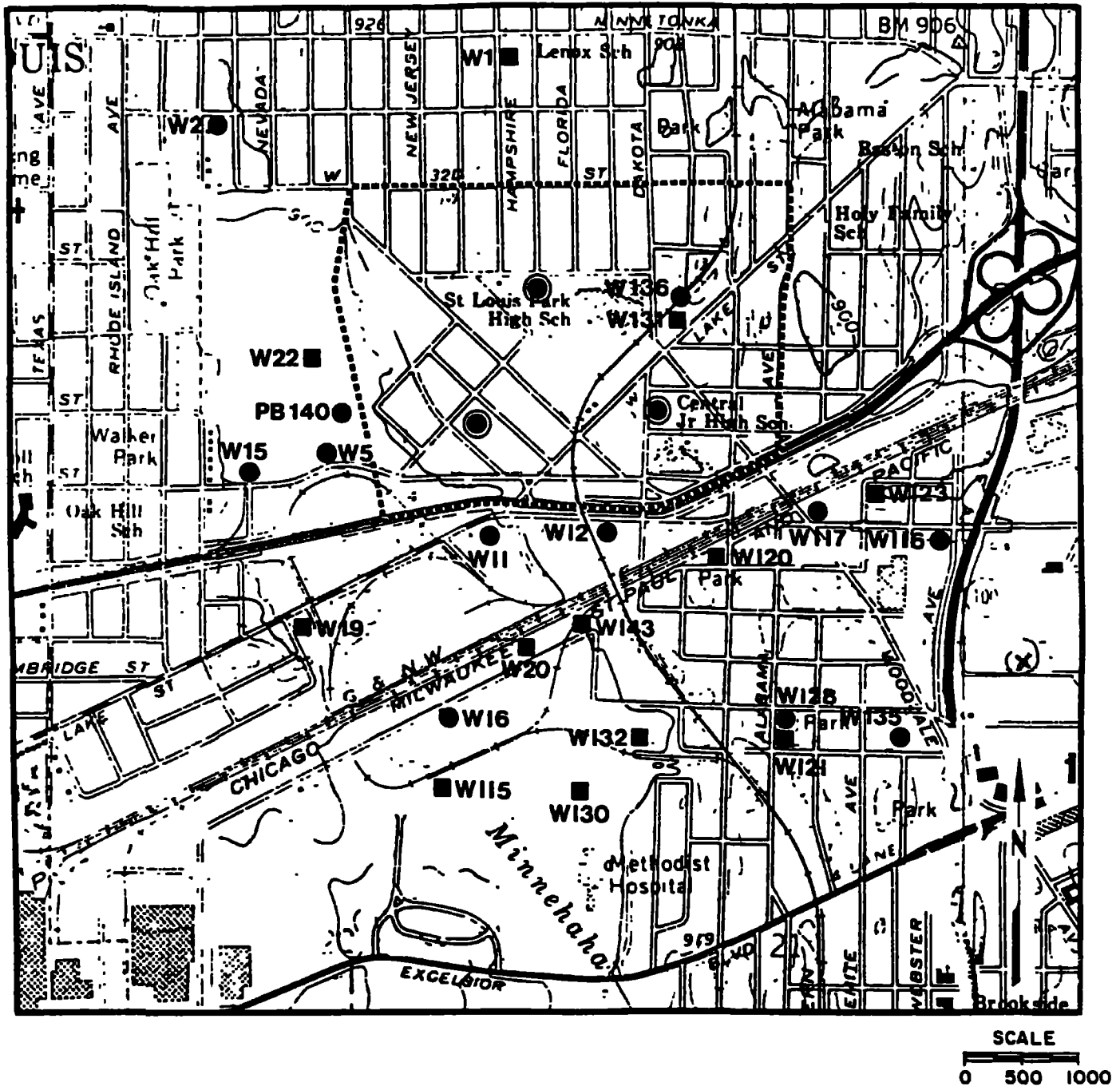
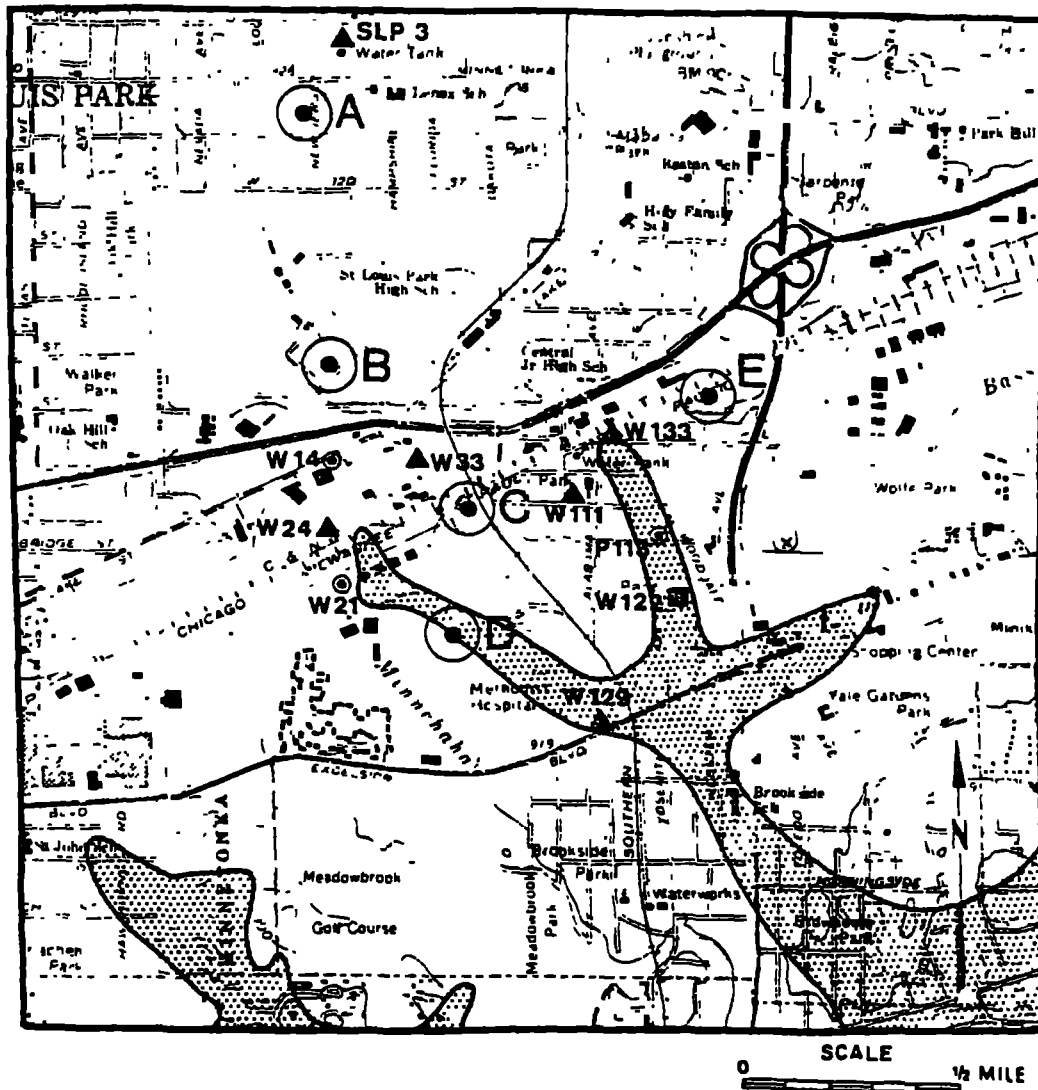


Figure 6-4 Location of Drift-Platteville Monitoring Wells

Reference: MGS, Miscellaneous Map Series,
M-57, Plate 1 of 2, Bedrock Geology,
by Bruce A. Bloomgren, 1985



EXPLANATION

- ▲ W33 LOCATION AND PROJECT WELL NUMBER**
- ▲ OBSERVATION WELL COMPLETED IN ST. PETER AQUIFER**
 - OBSERVATION WELL COMPLETED IN BASAL ST. PETER CONFINING BED**
 - PROPOSED ST. PETER MONITORING WELLS**
 - ◎ WELL IN WHICH WATER LEVELS WERE MONITORED WITH A DIGITAL RECORDER DURING PART OF 1978-81**
- ▨ BEDROCK VALLEY/CONTACT WHERE UNCONSOLIDATED DRIFT DEPOSITS OVERLIE ST. PETER SANDSTONE**

Figure 6-5 Location of St. Peter Monitoring Wells

- Document Number
- Page Number
- Total number of pages in document
- Revision number
- Revision date

When any of these documents are revised, the affected pages are reissued to all personnel listed as document holders with updated revision numbers and dates. Issuance of revisions is accompanied by explicit instructions as to which documents or portions of documents have become obsolete.

Control of, and accounting for documents generated during the course of the project is achieved by assigning the responsibility for document issuance and archiving. Table 6-3 lists the key documentation media for the project and corresponding responsible parties for issuance, execution and archiving.

Table 6-4 is a list of ERT Standard Operating Procedures applicable to the field sampling and field analysis portion of the project. These Standard Operating Procedures are contained in Appendix A. Procedures stated in the Site Management Plan or this QAPP which are different from those in the appended SOPs shall supercede these SOPs.

6.3 Sample Control Procedures and Chain of Custody

In addition to proper sample collection, preservation, storage and handling, appropriate sample identification procedures and chain of custody are necessary to help insure the validity of the data.

6.3.1 Sample Identification

Sample labels shall be completed for each sample, using waterproof ink, unless prohibited by weather conditions. For example, a logbook notation would explain that a pencil was used to fill out the sample tag because a ballpoint pen would not function in freezing weather. The information recorded on the sample label includes:

Sample Number - Unique coded sample identification number as described below.

Time - A four-digit number indicating the military time of collection.

Sampler - Signature of person collecting the sample.

TABLE 6-3
DOCUMENT CONTROL

<u>Item</u>	<u>Issued By</u>	<u>Issued To</u>	<u>Archived By</u>
Field Notebooks	Field Coordinator	Sampling Team	Field Coordinator
Field Equipment Calibration Forms	Field Coordinator	Sampling Team	Field Coordinator
Sample Logs	Field Coordinator	Sampling Team	Field Coordinator
Chain-of-Custody Forms	Lab Sample Custodian	Field Coordinator	Lab Sample Custodian
Sample Labels	Field Coordinator	Sampling Team	Lab Sample Custodian

TABLE 6-4
ERT STANDARD OPERATING PROCEDURE LIST

<u>Name</u>	<u>Title</u>
7320	Operation of Hydrolab
7510	Packaging and Shipment of Samples

Remarks - Any pertinent observations or further sample description.
The sample number includes three parts (source code, sampling point code, and date code) in the following sequence:

XXX-YYYYY-ZZZZZZ

XXX	= Source Code	
	GAC Plant	= GAC
	Mt. Simon-Hinckley Aquifer	= MSH
	Iron-ton-Galesville Aquifer	= IGV
	Prairie du Chien Jordan Aquifer	= PCJ
	St. Peter Aquifer	= STP
	Drift-Platteville Aquifer	= DPV
YYYYY	= Sampling Point Code	
	Well identification as abbreviated in Tables 6-1 and 6-2	
ZZZZ	= Date Code	
	Month, day, year	

After collection, identification, and preservation, the sample will be maintained under chain-of-custody procedures discussed below.

6.3.2 Chain-of-Custody Procedures

To maintain and document sample possession, chain-of-custody procedures will be followed. A sample is under custody if:

- It is in someone's possession, or
- It is in someone's view, after being in their possession, or
- It was in someone's possession and they locked it up to prevent tampering, or
- It is in a designated secure area.

TRANSFER OF CUSTODY AND SHIPMENT

1. Samples are accompanied by a Chain-of-Custody Record (Figure 6-6). When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the record. This record documents sample custody transfer from the sampler, often through another person, to the analyst at the laboratory.
2. Minimum information recorded on the chain-of-custody record in addition to the signatures and dates of all custodians will include:

- Sampling site identification
- Sampling date and time

Page: 29 of 125
Date: Jan. 1987
Number: QA E415
Revision: 0

CHAIN OF CUSTODY RECORD

[illegible]

- Chain-of-custody tape number
 - Identification of sample collector
 - Sample identification
 - Sample description (type and quantity)
 - Analyses to be performed.
3. Samples will be packaged properly for shipment and dispatched to the appropriate laboratory for analysis, with a separate custody record accompanying each shipment. Shipping containers will be sealed for shipment to the laboratory. Before sealing each container, select two pieces of chain-of-custody tape and enter their numbers on the chain-of-custody form (in your "relinquished by" signature box). The method of shipment, courier name(s) and other pertinent information are entered in the "Remarks" box. Then tear off the last copy of the form and place the original and remaining copies in the container. After the container is sealed, place the chain-of-custody tape over the seal on opposite corners of the container.
 4. Whenever samples are split with another laboratory, it is noted in the "Remarks" section. The note indicates with whom the samples are being split and is signed by both the sampler and recipient. If either party refuses a split sample, this will be noted and signed by both parties. The person relinquishing the samples to the facility or agency should request the signature of a representative of the appropriate party, acknowledging receipt of the samples. If a representative is unavailable or refuses to sign, this is noted in the "Remarks" space. When appropriate, as in the case where the representative is unavailable, the custody record should contain a statement that the samples were delivered to the designated location at the designated time.

6.3.3 Field Forms

In addition to sample labels and chain-of-custody forms, a bound field notebook will be maintained by the sample team leader to provide a daily record of significant events. All entries will be signed and dated. All members of the of the sampling team will use this notebook. The notebook will be kept as a permanent record.

6.4 Sampling Procedures - GAC Plant

Chain-of-custody forms will be completed and all samples shipped to ERT's laboratory by overnight delivery on the same day they are collected.

Sampling points will be flushed for at least five minutes before collecting a sample. Each PAH sample will be collected in four one-liter amber glass bottles, which should be filled and capped in succession. PAH sample bottles will not be rinsed before being filled. The lids of all sample bottles will be taped using plastic adhesive tape after they are capped.

The GAC treated water samples will have to be collected from two sample taps -- one for each column (see Figure 6-7). This will be done by filling two one-liter bottles from the first column sample tap and then two more bottles from the second (four from each for duplicate samples). No notations distinguishing the two taps will be made on the labels. All four PAH bottles will be extracted and the extracts composited for analysis.

Field blank samples will be prepared by transferring contaminant-free deionized water provided by ERT into sample bottles in a fashion as closely similar to actual sample collection as possible. Field blank sample bottles will be filled, capped and taped in succession with individual bottles open to the atmosphere for an equal time as for actual process samples. Field blanks will be prepared in the area in which GAC treated water samples are collected.

Duplicate samples will be obtained by filling eight 1-liter bottles at the sampling point by the procedure described above, splitting these into two groups of four bottles, and assigning a different sample number to each of the resulting four-bottle samples. All samples will be packed, cooled to a temperature less than 4°C, and shipped on the day they are collected. All sample handling, packaging and shipping will follow ERT's Standard Operating Procedure No. 7510 (Appendix A).

The sampling team must recognize that great care is required to collect samples for part-per-trillion-level PAH analysis that are free from outside contamination. PAH compounds are present in cigarette smoke, engine exhaust and many petroleum derived oils, among other sources. There will be no smoking anywhere in the GAC treatment building on a day on which PAH samples are to be collected until the samples have been collected, sealed and packaged for shipment. Similarly, no vehicles will enter the GAC treatment building and the large access door will stay closed on sampling days. Disposable gloves will be worn when collecting, handling and packaging samples. Sample bottles will remain in closed shipping coolers until they are needed, and will be packaged and sealed for shipment as soon as possible after sampling.

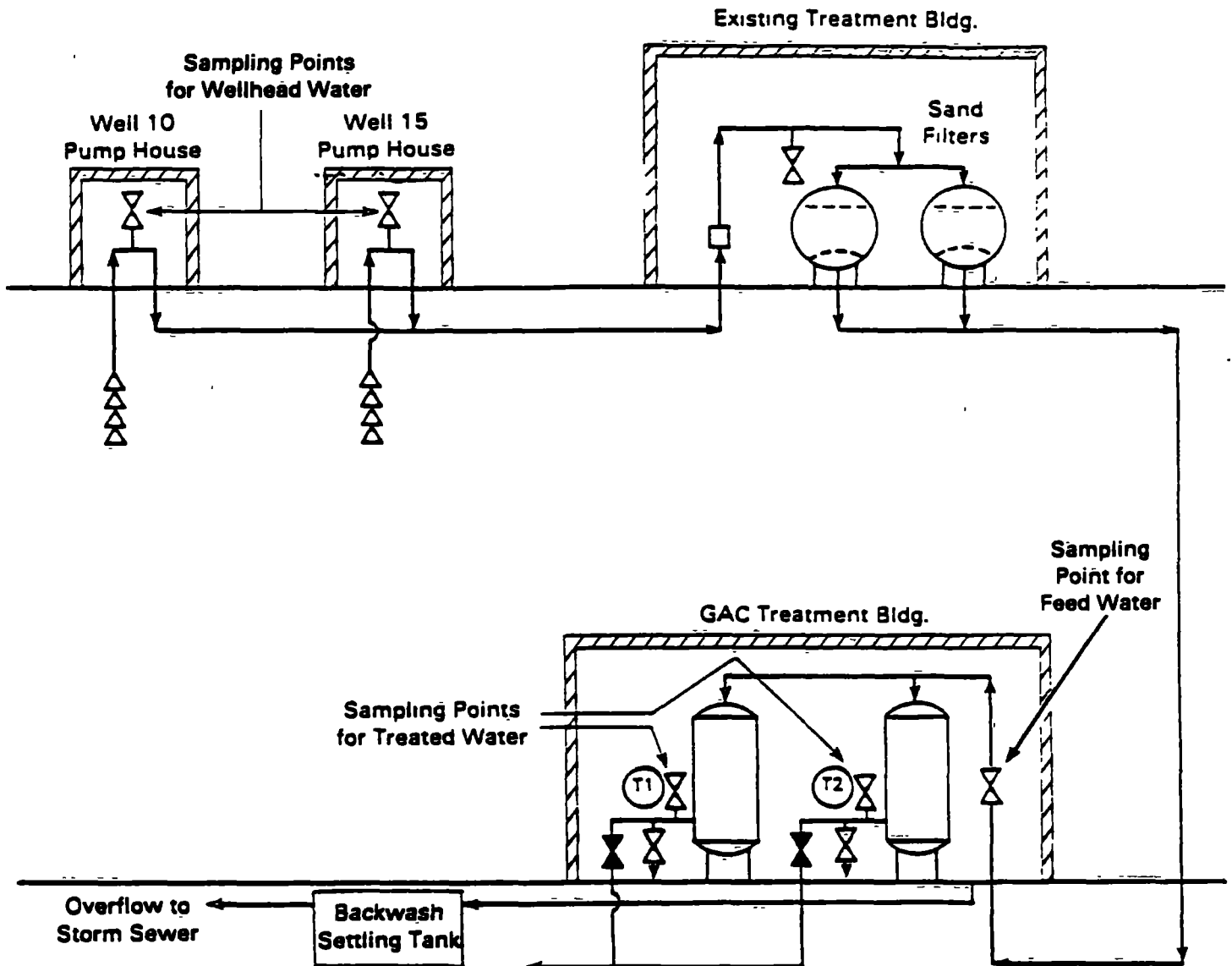


Figure 6-7 Sampling Locations

6.5 Ground-water Sampling and Water Level Measurements

Ground water samples will be collected and water level measured in accordance with the procedures outlined in the Site Management Plan and this Quality Assurance Project Plan. The wells involved in the monitoring program include municipal and commercial wells, piezometers and groundwater monitoring wells (see Table 6-2). Sampling procedures to accommodate the dimensions and configuration of each type of well are described below. Further details on well dimensions, water level measurements and sample acquisition strategies are given in the Site Management Plan.

The importance of proper sampling of wells cannot be over-emphasized. Even though the well being sampled may be correctly located and constructed, special precautions must be taken to ensure that the sample taken from that well is representative of the ground water at that location and that the sample is neither altered nor contaminated by the sampling and handling procedure. Sample collection will always proceed from the less contaminated sampling points to the monitoring wells containing progressively higher concentrations of PAH or phenolics.

6.5.1 Decontamination

The decontamination procedure to be used on sampling equipment which comes into contact with the groundwater is as follows:

- scrub with soap and water,
- rinse with deionized water,
- rinse with acetone,
- rinse with hexane,
- rinse with acetone,
- rinse with deionized water, and
- air dry for 15 minutes.

6.5.2 Field Blanks

Field blank samples will be prepared by transferring contaminant-free deionized water, provided by ERT, into sample bottles in a fashion as closely similar to actual sample collection as possible. This will involve collecting samples through any non-dedicated sample equipment that is decontaminated between samples. Field blank sample bottles will be filled, capped and taped in succession with individual bottles open to the atmosphere for an equal time as for actual process samples. Field blanks will be prepared in the area where samples are being collected at a rate of one per day or where more than ten samples are collected in a day at a rate of one field blank per ten samples.

6.5.3 Sample Containers (See Table 6-5)

For PAH and Phenolics, 1 liter amber glass bottles will be used. Caps will be fitted with pre-cleaned Teflon liners. Four bottles are required for each PAH sample collected. One bottle is required for phenolics.

Bottles will be prepared as follows:

1. Wash bottles with hot detergent water.
2. Rinse thoroughly with tap water followed by three or more rinses with organic-free water.
3. Rinse with Burdick & Jackson quality redistilled acetone, followed by equivalent quality methylene chloride.
4. Allow to air dry in a contaminant free area.
5. Caps and liners must be washed and rinsed also.

Bottles should be stored and shipped with the Teflon-lined caps securely fastened.

For parameters on the expanded list for the Northern Area of the Drift and Platteville Aquifer, 1-liter amber glass bottles will again be used for the acid and base/neutral extractable organics. Each volatile organics sample will be collected in two forty-milliliter VOA vials. The vials will be prepared in the laboratory before sampling by baking at 110°C for approximately 15 minutes. Samples for metals and ions will be collected in 1-liter polyethylene cubitainers.

TABLE 6-5
SAMPLE CONTAINERS, PRESERVATION PROCEDURES, AND
MAXIMUM HOLDING TIMES

<u>Parameter</u>	<u>Containers</u>	<u>Preservation</u> ¹	<u>Maximum Holding Time</u> ²
Water:			
PAH (PPT)	Four 1-liter amber glass bottles, Teflon-lined caps	cool, 4°C; protect from light	7 days (until extraction), 40 days after extraction
PAH (PPB)	Two 1-liter amber glass bottles, Teflon-lined caps	cool, 4°C, protect from light	7 days (until extraction), 40 days after extraction
Phenolics	One 1-liter amber glass bottle,	cool, 4°C	7 days (until extraction), 40 days after extraction
Acid, Base/Neutral Extractables	Two 1-liter amber glass bottles, Teflon-lined cap	cool, 4°C (0.008% Na ₂ S ₂ O ₃ , if residual Cl is present)	7 days (until extraction), 40 days after extraction
Volatile Organics	Three 40-ml VOA vials, Teflon septum	cool, 4°C	14 days
Metals	Two 1-liter cubitainers	HNO ₃ to pH <2	6 months
SO ₄ and Cl	One 1-liter cubitainer	cool, 4°C	28 days
Mercury	One 1-liter cubitainer	HNO ₃ to pH <2	28 days
Cyanide	One 1-liter cubitainer	cool, 4°C; NaOH to pH >12	14 days
Total phenols	One 1-liter amber glass bottle	cool, 4°C; H ₂ SO ₄ to pH <2	28 days
NH ₃	One 1-liter cubitainer	cool, 4°C; H ₂ SO ₄ to pH <2	28 days
Na	One 1-liter cubitainer	HNO ₃ to pH <2	6 months

Ref: Federal Register Guidelines/Vol.49, No.209/Friday, October 26, 1984/p. 43260.

¹ Sample preservation will be performed immediately upon sample collection.

² Samples will be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid.

6.5.4 Sample Collection - Monitoring Wells

Monitoring wells having a riser pipe inside diameter of 2 inches or greater will be purged and sampled using a stainless steel submersible pump with teflon seals and fittings. The pump discharge will be brought to the surface using a tygon tube. One tube will be dedicated to each well.

The submersible pump will be decontaminated before use and between sampling points as described in Section 6.5.1.

During the purging of each well, temperature, pH and specific conductance of the purge water will be monitored using a Hydrolab water quality monitor (or equivalent). Readings will be taken once per well volume. Stabilization of these readings will indicate that purging is complete and sampling may commence. All pump discharge not containerized as samples will be disposed of as outlined in the Site Management Plan.

Samples are collected by filling each of the appropriate sample containers in rapid succession, without prerinsing the containers with sample. The bottle is held under the sample stream without allowing the mouth of the bottle to come in contact with tubing, pipes, etc and filled completely, and the cap securely tightened. Amber glass bottles and VOA vials are checked for air and if air is visible, the cap removed and more sample added. All sample labels will be checked for completeness, sample custody forms completed and a description of the sampling event recorded in the field notebook.

6.5.5 Sample Collection - Piezometers

Piezometers, having a riser pipe inside diameter of less than 4 inches, will be purged and sampled with a peristaltic pump and Tygon tubing. Pump decontamination will not be required, as the water to be sampled will never come in contact with the pump. Well purging and purge water monitoring for stabilization of temperature, pH and specific conductance will be performed as described in 6.4.4. Sample collection and containerization will also be as described in 6.4.4.

6.5.6 Sample Collection - Pumping Wells

Samples will be collected from municipal and private pumping wells in accordance with the procedures given in the Site Management Plan. Municipal well samples will be acquired from a sampling point as close to the well head as possible. The sampling port will be purged for at least five minutes before a sample is collected. Procedures for sample containerization will be as described in 6.4.4.

6.6 Sample Preservation, Shipment and Storage

The samples will be iced or refrigerated at 4°C from the time of collection until extraction. PAH's are known to be light sensitive; therefore, samples will be stored in amber bottles and kept away from prolonged exposure to light. All samples will be extracted within seven days of collection, and analysis completed within forty days following extraction.

Samples will be protected from breakage and shipped in coolers at a temperature of 4°C or less. An overnight carrier will be selected to insure delivery at the laboratory within 24-36 hours after collection.

Samples received at the laboratory will be checked for leakage and a notation made regarding sample temperature at time of receipt. All samples should be stored in an organic-free refrigerator at 4°C. Storage refrigerators will be kept locked to prevent unauthorized entry and to satisfy chain-of-custody requirements.

6.7 Field Measurement Equipment

All field measurement equipment will be controlled to ensure that measurements obtained are accurate and defensible. Table 6-6 summarizes the parameters to be monitored, the instruments to be used for each measurement, procedures including calibration and frequency, and quality control criteria.

In addition, these measurement devices will be issued through a formal equipment tracking system and operated by trained personnel, in accordance with the appropriate SOPs.

6.8 Duplicate Samples

Duplicate samples will be collected by alternately filling sample bottles from the source being sampled. For four liter sample collection one bottle will be filled for the sample, then one bottle for the duplicate, then a second bottle for the sample and then a second bottle for the duplicate, etc. Duplicates will be taken for each analysis type and each sample type, at a rate of one duplicate sample being collected for each ten samples, with a minimum of one duplicate for any sample batch. There are two sample types for this program: GAC Plant treated water and groundwater. For purposes of fulfilling the 10% duplicate requirement, all the sampling points shown on Table 6-2 are the same sample type.

TABLE 6-6
FIELD MEASUREMENT EQUIPMENT QUALITY CONTROL

<u>Device</u>	<u>Calibration</u>	<u>Routine Check</u>		<u>Control Limits</u>
		<u>Method</u>	<u>Frequency</u>	
pH Meter (Hydrolab)	Standardize in three or more standard buffer solutions	Calibration check-analyze standard buffer solution	after every sample	± 0.1 pH units
		Analyze duplicates	after every sample	± 0.1 pH units
Conductivity Meter (Hydrolab)	Standardize using two or more KCL solutions	Calibration check-analyze standard KCL solution	1/10 Samples	$\pm 10\%$ full scale
		Analyze duplicates	1/10 Samples	$\pm 10\%$ full scale

7. SAMPLE CUSTODY

The ERT Analytical Laboratory operates under a formal quality control program. The Chain-of-Custody contains three major elements; the field sampling, the laboratory analysis and the final evidence file. Section 6.3 discusses the field sampling aspects. This section covers quality related activities applicable to the St. Louis Park Groundwater Study from the receipt of samples at the laboratory through the issuance of validated analytical data and the storage of data in the final evidence file.

7.1 Chain-of-Custody

When samples are received into the laboratory the Sample Custodian will verify their integrity as they are unpacked and will explicitly state in the log-in records whether the chain-of-custody seal is intact, whether the sample is received intact or broken, and whether the sample is appropriately identified. If the integrity requirements are met, or when any discrepancies are resolved, ERT assigns the sample a laboratory control number, stores the sample in a refrigerator and enters the pertinent information into the sample log. Once the samples are in the laboratory, a sample usage log is maintained on the LIMS computer to track the transport and use of each sample within the laboratory.

The laboratory will retain a copy of each chain-of-custody record, with the shipper's waybill or air bill attached. After sample log-in, a second copy of the chain-of-custody record will be sent to the Field Coordinator, indicating sample receipt and associated ERT laboratory number. The laboratory will use a Sample Usage Log Sheet (Figure 7-1) to track sample usage through preparation and analysis stages. Spaces are provided to document the initial sample size stored, who, when, for what purpose, and how much of a sample was removed and when and who returned the remainder to its assigned storage location. After disposition, the final copy of the chain-of-custody will be sent documenting the disposition method and date.

7.2 Recordkeeping

In addition to sample chain-of-custody, the laboratory will maintain the necessary documentation to reconstruct the entire process of sample preparation through analysis and report generation. This documentation is found in logbooks, data packages and stored on tape.

The logbooks and information they contain are listed below.

- Chemical Inventory Log - ERT Chemical Inventory control number, compound/reagent name, manufacturer, lot number, grade, date received, expiration date and disposition date.

Figure 7-1 Sample Usage Log Sheet

ERT

SAMPLE USAGE LOG

Page No. 603

Date_____

By _____

ERT Lab No.._____

Storage Location _____

Client: _____

Contact _____

Project No.._____

Sample Matrix _____

Sample Type **Haz** **Waste** **Trace**

Sample Container: _____

Approximate Sample Size (gms. mls) _____

Analyses:_____

[illegible]

- Reference Standard Inventory Log - ERT Reference Standard Inventory control number, compound name, manufacturer, lot number, concentration, solvent, date received, expiration and disposition date.
- Super Stock Preparation Log - ERT Super Stock Standard number; neat compound and solvent or carrier name and their pertinent data such as lot number, manufacturer, percent activity, expiration date (if any), weights and volumes taken and balance used; final stock standard concentration, expiration date of standard, storage requirements and location, preparation date and time, preparer's initials, approval signature and date.
- Mixed and/or Dilution Standards Log - ERT Mixed Standard number; pertinent information of Super Stock Standards used such as standard numbers, concentration, preparation date, volume taken, volume diluted to and solvent used (including lot number, manufacturer); mixed and/or dilution standards preparer's initials, date, final concentration of each component, storage, location, approval signature (of supervisor) and date disposed.
- Instrument Maintenance Log - initialed and dated entries pertaining to instrument set-up, routine preventative maintenance, and instrumental malfunction and resolutions.
- Instrument Sample Sequence Log - initialed and dated listing of standards and samples analyzed.
- Instrument Tuning Log - initialed and dated mass intensity listings of daily GC/MS DFTPP tunes.

The data package contains only data pertinent to the individual project. This package is filed alphabetically by project and date and includes the following records:

- Data Approval Form - a form which lists the contents of the Data Package and routes the data review process (Figure 7-2).
- Out-of-Control Event Form - a form which describes any out-of-control events which may affect the quality of data to be reported and explains the causes and corrective actions taken (Figure 7-3).
- Sample Receipt Checklist - a checklist describing sample integrity upon receipt into the laboratory (Figure 7-4).
- Initial Page - a sheet which lists the signatures and initials of all personnel involved in the preparation and review of the Data Package (Figure 7-5).
- Daily Log Sheet - a log containing daily entries or comments pertaining to any part of sample preparation and/or analysis, which are not described on the other forms such as instrument fluctuations and tuning or where the sample analysis sequence can be found, etc. (Figure 7-6)

Figure 7-2 Data Approval Form

ERT

NO.

QUALITY ASSURANCE FORM

SUBJECT: DATA APPROVAL

CLIENT: _____ PROJECT NO: _____

ANALYSIS PARAMETER(S): _____

: _____

PLEASE REVIEW AND APPROVE/DISAPPROVE THE ATTACHED DATA SHEET(S) AND/OR NOTEBOOK(S) AND ROUTE THROUGH THE PERSONNEL LISTED BELOW. IF YOU DISAPPROVE OF ANYTHING PLEASE RETURN THIS PACKAGE TO THE INITIATOR. THE CORRECTIONS WILL BE MADE AND THE APPROVAL PROCESS WILL BEGIN AGAIN.

INCLUDED IN THIS DATA PACKAGE (PLEASE LIST BELOW):

ROUTING		DATE	SIGNATURE	
TITLE	NAME		APPROVAL	DISAPPROVAL /SEE SIDE 2
INITIATOR				
Q.A. UNIT				

(OVER)

Figure 7-3 Out-of-Control Event Form

Date _____ Time _____ Analyst _____

Method _____ Matrix _____

Initials of individual initially notified _____

Suspect lab numbers _____

Out-of-control lab numbers _____

Indication of out-of-control event _____

Cause determined _____

Action taken _____

Date and time QAC notified _____

Date and time control resumed _____

Precision criteria met _____ Accuracy criteria met _____

Reanalysis of data completed _____

Figure 7-4 Sample Receipt Check List

ERT

SAMPLE RECEIPT CHECK LIST

Client:

COC Record #(s)

Matrix	Container	ERT #(s)

1. Were samples shipped or hand-delivered?

Notes:

Yes No
☐ ☐

2. Was COC record present upon receipt of samples?

Notes:

Yes No
☐ ☐

3. Was COC tape present/unbroken on outer package?

Notes:

4. Were samples received ambient or chilled?

Notes:

Yes No
☐ ☐

5. Were any samples received broken/leaking (improperly sealed)?

Notes:

Yes No
☐ ☐

6. Were samples properly preserved?

Notes:

Yes No
☐ ☐

7. Were COC types present/unbroken on samples?

Notes:

Yes No
☐ ☐

8. Any discrepancies between sample labels and COC records?

Notes:

Yes No
☐ ☐

9. Were samples received within holding times?

Notes:

Additional Comments:

Samples inspected and logged in by _____ Date: _____

QUALITY ASSURANCE PROJECT PLAN

Page: 46 of 125
Date: Jan. 1987
Number: QA E415
Revision: 0

Figure 7-6 Daily Log Sheet

ERT

PAGE : _____

QUALITY ASSURANCE FORM -

SUBJECT: DAILY LOG DATE AND SIGN EACH ENTRY

This image shows a single sheet of white paper with horizontal blue or grey ruling lines. The lines are evenly spaced and run across the width of the page. There is no handwriting or other markings on the paper.

- Serial Dilution Sheet - a sheet which is used to describe how dilutions were made from mixed standards to be used as calibration standards or in-house spiking solutions. The following is required: Information about the super stock standards such as parameter, concentration, date prepared, ERT stock standard number, etc. and information about the serial standard preparation such as volume of standard taken, volume diluted to, solvent used, final concentrations, storage location, who prepared it and the date prepared (Figure 7-7).
- Analytical Results of QA/QC Fortified Samples (Matrix Spikes) - on this sheet one records pertinent preparation information for spiking samples (GAC treated water) such as volume or weight of sample spiked, concentration of standard used for spiking, and volume of spike used. From this information, one can then calculate the expected concentration of parameter spiked into the matrix spike sample (Figure 7-8).

In addition to these forms, a Data Package will contain other pertinent information such as daily instrument calibration, check standard results, chromatographic charts, computer printouts, references to other logbook entries and correspondences. Copies of all GC/MS raw data files are also transferred to magnetic storage media.

7.3 Final Evidence Files

All data files are maintained in a final evidence file. The ERT laboratory stores all final evidence files in a locked and alarmed sample data vault. Access to the final evidence files is limited to authorized laboratory personnel. Final evidence files for this program will be stored for the life of the consent decree.

Page: 48 of 125
Date: Jan. 1987
Number: QA E415
Revision: 0

Revision: 0

[illegible]

ERT

QUALITY ASSURANCE FORM

Pago

SUBJECT ANALYTICAL RESULTS OF QA/QC FORTIFIED (OVERSPIKED) SAMPLES

Client _____ Sample Matrix _____

Project No _____ **Analyte** _____

[illegible]

QUALITY ASSURANCE PROJECT PLAN

Page: 49 of 125
Date: Jan. 1987
Number: QA E415
Revision: 0

Figure 7-8 Analytical Results of QA/QC Fortified (Overspiked) Samples Sheet

8. CALIBRATION PROCEDURES

8.1 Low-Level (ppt) Analysis of PAH and Heterocycles

Prior to use of the method for low level analysis of PAH and Heterocycles, a five-point response factor calibration curve must be established showing the linear range of the analysis. For every 12 hours of GC/MS analysis, the mass spectrometer response for each PAH or heterocycle relative to the internal standard is determined, as described in the Calculations Section, using daily check standards at concentrations of 40 ng/mL. Daily response factors for each compound must be compared to the initial calibration curve. If the daily response factors are within ± 35 percent of the corresponding calibration curve value the analysis may proceed. If, for any analyte, the daily response factor is not within ± 35 percent of the corresponding calibration curve value, a five-point calibration curve must be repeated for that compound prior to the analysis of samples.

Chromatographic peak location criteria will be established using relative retention time. An initial determination of retention times for each PAH or heterocycle relative to its respective internal standard (Table 8-1) will be made using five-point calibration standards. Representative average relative retention times, standard deviations and 95 percent confidence limits are presented in Table 8-2. Relative retention times of daily check standards must be within the 95 percent confidence limits calculated from the calibration standards for each PAH or heterocyclic compound. In addition, sample component relative retention times must be within ± 0.1 relative retention time units of the standard component relative retention time.

8.1.1 Daily GC/MS Performance Tests

At the beginning of each 12 hour shift that analyses are to be performed, the GC/MS system must be checked to see that acceptable performance criteria are achieved for decafluorotriphenylphosphine (DFTPP). This DFTPP performance test requires the following instrumental parameters:

Electron Energy 70 volts (nominal)
Mass Range - 35 to 450 amu
Scan Time - 1.0 sec.

At the beginning of each 12 hour shift, inject 2 μ L (50 ng) of DFTPP standard solution. Obtain a background corrected mass spectrum of DFTPP and check that all the key ion criteria in Table 8-3 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved.

TABLE 8-1
COMPOUNDS AND MS QUANTITATION MASS IONS

<u>Compound</u>	<u>Quantitation Mass Ion</u>	<u>Confirmation Ion (% Abundance)</u>	<u>Internal Standard Reference</u>
<u>Polynuclear Aromatic Hydrocarbons (PAH)</u>			
Naphthalene	128	102 (20)	1
Acenaphthylene	152	151 (20)	1
Acenaphthene	154	153 (90)	1
Fluorene	166	165 (80)	2
Phenanthrene	178	176 (20)	2
Anthracene	178	176 (20)	2
Fluoranthene	202	200 (20)	2
Pyrene	202	200 (20)	2
Benzo(a)anthracene	228	226 (20)	3
Chrysene	228	226 (20)	3
Benzofluoranthenes	252	250 (25)	3
Benzo(a)pyrene	252	250 (25)	3
Indeno(1,2,3,cd)pyrene	276	274 (20)	3
Dibenzo(a,h)anthracene	278	276 (20)	3
Benzo(g,h,i)perylene	276	274 (20)	3
<u>Internal Standards</u>			
1) Acenaphthene-d10	164		-
2) Phenanthrene-d10	188		-
3) Benzo(a)pyrene-d12	264		-
<u>Surrogates</u>			
1) Naphthalene-d8	136		1
2) Fluorene-d10	176		2
3) Chrysene-d12	240		3

TABLE 8-1 (Continued)
COMPOUNDS AND MS QUANTITATION MASS IONS

<u>Compound</u>	<u>Quantitation Mass Ion</u>	<u>Confirmation Ion (% Abundance)</u>	<u>Internal Standard Reference</u>
<u>Heterocycles and Other PAH</u>			
Indene	116	115 (90)	1
Indole	117	90 (40)	1
2,3-dihydroindene	118	117 (50)	1
2,3-benzofuran	118	90 (40)	1
Quinoline	129	102 (30)	2
Benzo(b)thiophene	134	--	2
2-methyl naphthalene	141	115 (40)	2
1-methyl naphthalene	141	115 (40)	2
Biphenyl	154	153 (30)	3
Carbazole	167	166 (25)	3
Dibenzofuran	168	139 (25)	3
Acridine	179	178 (25)	3
Dibenzothiophene	184	139 (20)	3
Perylene	252	250 (30)	3
Benzo(e)pyrene	252	250 (30)	3
<u>Internal Standards</u>			
1) Acenaphthene-d10	164		-
2) Phenanthrene-d10	188		-
3) Benzo(a)pyrene-d12	264		-
<u>Surrogates</u>			
1) Naphthalene-d8	136		1
2) Flourene-d10	176		2
3) Chrysene-d12	240		3

TABLE 8-2

RELATIVE RETENTION TIMES AND CONFIDENCE LIMITS FOR THE COMPOUNDS
ASSOCIATED WITH THE LOW LEVEL PAH AND HETEROCYCLE METHODOLOGY

<u>Group I</u>	<u>Avg. RRT</u>	<u>SD</u>	<u>% RSD</u>	<u>95% Confidence Limits</u>
benzofuran	0.550	0.015	2.807	0.520-0.580
dihydroindene	0.590	0.016	2.765	0.558-0.622
indene	0.598	0.016	2.699	0.566-0.630
Naphthalene-d8 (Surr.)	0.733	0.017	2.289	0.699-0.767
Naphthalene	0.735	0.017	2.289	0.701-0.769
Benzo(b)thiophene	0.743	0.017	2.258	0.709-0.777
Quinoline	0.783	0.017	2.140	0.749-0.817
Indole	0.824	0.018	2.167	0.788-0.860
2-methyl	0.832	0.017	2.084	0.798-0.866
1-methyl	0.848	0.017	2.055	0.814-0.882
Biphenyl	0.901	0.017	1.921	0.867-0.935
Acenaphthylene	0.962	0.018	1.822	0.927-0.988
Acenaphthene	0.988	0.018	1.849	0.952-1.024
Dibenzofuran	1.011	0.018	1.791	0.975-1.047
 Group II				
Fluorene-d10 (Surr.)	0.872	0.015	1.735	0.842-0.902
Fluorene	0.875	0.015	1.745	0.845-0.905
Dibenzothiophene	0.974	0.016	1.617	0.942-1.006
Phenanthrene	0.988	0.016	1.589	0.956-1.020
Anthracene	0.994	0.016	1.597	0.962-1.026
Acridine	0.999	0.016	1.572	0.967-1.031
Carbazole	1.013	0.015	1.487	0.983-1.043
Fluoranthene	1.130	0.017	1.461	1.096-1.164
Pyrene-d10 (Surr.)	1.155	0.017	1.444	1.121-1.189
Pyrene	1.157	0.017	1.443	1.123-1.191
 Group III				
Benz(a)anthracene	0.873	0.012	1.325	0.849-0.897
Chrysene-d12 (Surr.)	0.874	0.012	1.320	0.850-0.898
Chrysene	0.876	0.012	1.320	0.852-0.900
Benzo(a)fluoranthene	0.960	0.014	1.501	0.932-0.988
Benzo(e)pyrene	0.984	0.016	1.590	0.952-1.016
Benzo(a)pyrene	0.988	0.016	1.615	0.956-1.020
Perylene-d12 (Surr.)	0.944	0.016	1.634	0.962-1.026
Perylene	0.996	0.016	1.644	0.964-1.028
Indeno (123,cd)pyrene	1.114	0.025	2.276	1.064-1.164
Dibenz(ah)anthracene	1.113	0.031	2.743	1.051-1.175
Benzo(ghi)perylene	1.149	0.028	2.422	1.093-1.205

TABLE 8-3
DFTPP ION ABUNDANCE CRITERIA

<u>Mass</u>	<u>Ion Abundance Criteria</u>
51	30 to 60 percent of mass 198
68	less than 2 percent of mass 69
70	less than 2 percent of mass 69
127	40 to 60 percent of mass 198
197	less than 1 percent of mass 198
198	base peak, 100 percent
199	5 to 9 percent of mass 198
275	10 to 30 percent of mass 198
365	greater than 1 percent of mass 198
441	present but less than mass 443
442	greater than 40 percent of mass 198
443	17 to 23 percent of mass 442

8.1.2 Gas Chromatography/Mass Spectrometry Analysis

Just prior to analysis a 125 μ l aliquot of internal standard solution is transferred to the sample vial using a 250 μ L syringe, giving a final internal standard concentration of approximately 40 ng/mL in the extract. Representative aliquots are injected into the capillary column of the gas chromatograph using the following conditions:

Injector Temp - 290°C
Transfer Line Temp - 310°C
Initial Oven Temp - 35°C
Initial Hold Time - 2 min.
Ramp Rate - 10°C/min.
Final Temperature - 310°C

The effluent from the GC capillary column is fed directly into the ion source of the mass spectrometer. The MS is operated in the selected ion monitoring (SIM) mode using appropriate windows to include the quantitation and confirmation masses of each PAH or heterocycle as shown in Table 8-1. The time programmed SIM acquisition windows are listed in Table 8-4. Each SIM sequence is acquired at a total scan speed of 1.1 seconds per scan. Typical retention behavior of the combined PAH and heterocycle analytes and corresponding SIM sequences are shown in Table 8-5. For all compounds detected at a concentration above the MDL, a check is made to insure the confirmation ion is present.

Calculations

The following formula is used to calculate the response factors of the internal standard to each of the calibration standards.

$$RF = (A_s C_{is}) / (A_{is} C_s)$$

where:

A_s = Area of the characteristic ion for the parameter to be measured.
 A_{is} = Area of the characteristic ion for the internal standard.
 C_{is} = Concentration of the internal standard, (ng/mL).
 C_s = Concentration of the parameter to be measured, (ng/mL).

Based on these response factors, sample extract concentration for each PAH is calculated using the following formula.

TABLE 8-4
SELECTED ION MONITORING (SIM) SEQUENCE FOR
PAH AND HETEROOCYCLES

<u>Sequence #</u>	<u>M/Z Scanned</u>	<u>Scan # Range</u>	<u>Start Time (Min)</u>
1	90, 115, 116, 117, 118	300-499	5.50
2	102, 128, 129, 134, 136	500-599	9.17
3	90, 115, 117, 141, 153, 154	600-719	11.00
4	139, 151, 152, 153, 154, 164, 165, 166, 168, 176	720-899	13.20
5	139, 166, 167, 176, 178, 179, 184, 188	900-1049	16.50
6	200, 202, 212	1050-1249	19.25
7	226, 228, 240	1250-1399	22.92
8	250, 252, 264	1400-1649	25.67
9	274, 276, 278	1650-1850	30.25

TABLE 8-5

GC RETENTION BEHAVIOR FOR PAH AND HETEROCYCLES

<u>Compound</u>	<u>M/Z</u>	<u>Retention Scan Number</u>	<u>SIM Sequence #</u>
2,3-benzofuran	118	383	1
2,3-dihydroindene	118	420	1
Indene	116	429	1
Napthalene-d8 (Surr.)	136	548	2
Napthalene	128	551	2
Benzo(b)thiophene	134	557	2
Quinoline	129	593	2
Indole	117	635	3
2-methylnapthalene	141	640	3
1-methylnapthalene	141	653	3
Biphenyl	154	703	3
Acenaphthylene	152	756	4
Acenaphthene-d10 (IS-1)	164	776	4
Acenaphthene	154	781	4
Dibenzofuran	168	802	4
Fluorene-d10 (Surr.)	176	843	4
Fluorene	166	848	4
Dibenzothiophene	184	956	5
Phenanthrene-d10 (IS-2)	188	970	5
Phenanthrene	178	974	5
Anthracene	178	980	5
Acridine	179	985	5
Carbazole	167	1004	5
Fluoranthene	202	1134	6
Pyrene	202	1162	6
Benzo(a)anthracene	228	1333	7
Chrysene-d12 (Surr.)	240	1335	7
Chrysene	228	1339	7
Benzofluoranthenes	252	1496	8
Benzo(e)pyrene	252	1536	8
Benzo(a)pyrene-d12 (IS-3)	264	1539	8
Benzo(a)pyrene	252	1543	8
Perylene	252	1546	8
Indeno (1,2,3-cd)pyrene	276	1713	9
Dibenz(a,h)Anthracene	278	1718	9
Benzo(g,h,i)Perylene	276	1750	9

$$C_e = \frac{(A_s)(I_s)}{(A_{is})(RF)}$$

where:

C_e = Sample extract concentration (ng/ml)

A_s = Area of the characteristic ion for the parameter to be measured.

A_{is} = Area of the characteristic ion for the internal standard.

I_s = Amount of internal standard added to each extract (ng/mL).

The actual sample concentration (C) for each compound is calculated by the following formula:

$$C = (C_e) \times \left(\frac{V_E}{V_S} \right),$$

where

C = Concentration of sample (ng/l)

V_E = The final extract volume (mL), and

V_S = The original volume of sample extracted (L).

8.2 Extended Analyses for Carcinogenic PAH in GAC Plant

Prior to use of the low-level method, a five-point response factor calibration curve will be established showing the linear range of the analysis for the compounds listed in Table 8-6. For every 12 hours of GC/MS analysis, the mass spectrometer response for each PAH relative to the internal standard is determined, as described in the Calculations Section, using daily check standards at concentrations of 40 ng/mL. Daily response factors for each compound must be compared to the initial calibration curve. If the daily response factors are within ± 35 percent of the corresponding calibration curve value the analysis may proceed. If, for any analyte, the daily response factor is not within ± 35 percent of the corresponding calibration curve value, a five-point calibration curve must be repeated for that compound prior to the analysis of samples.

Chromatographic peak location criteria will be established using relative retention time. An initial determination of retention times for each PAH will be made using five-point calibration standards. Sample component relative retention times must be within ± 0.1 relative retention time units of the standard component relative retention time.

TABLE 8-6
EXTENDED ANALYSIS CARCINOGENIC PAH

<u>Compound</u>	<u>Quantitation Mass</u>
benzo(c)phenanthrene	226
dibenz(a,c)anthracene	278
dibenzo(a,e)pyrene	276
dibenzo(a,h)pyrene	276
dibenzo(a,i)pyrene	276
7,12-dimethylbenz(a)anthracene	256
3-methylcholanthrene	268

8.2.1 Daily GC/MS Performance Tests

At the beginning of each 12 hour shift that analyses are to be performed, the GC/MS system must be checked to see that acceptable performance criteria are achieved for DFTPP. This DFTPP performance test requires the following instrumental parameters:

Electron Energy 70 volts (nominal)

Mass Range - 35 to 450 amu

Scan Time - 1.0 sec.

At the beginning of each 12 hour shift, inject 2 μ L (50 ng) of DFTPP standard solution. Obtain a background corrected mass spectrum of DFTPP and check that all the key ion criteria in Table 8-3 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved.

8.2.2 Gas Chromatography/Mass Spectrometry Analysis

Representative aliquots are re-injected into the capillary column of the gas chromatograph using the following conditions:

Injector Temp - 290°C

Transfer Line Temp - 310°C

Initial Oven Temp - 35°C

Initial Hold Time - 2 min.

Ramp Rate - 10°C/min.

Final Temperature - 310°C

The effluent from the GC capillary column is fed directly into the ion source of the mass spectrometer. The MS is operated in the selected ion monitoring (SIM) mode using appropriate windows to include the quantitation masses of each PAH as shown in Table 8-6. The time programmed SIM acquisition is acquired at a total scan speed of 1.1 seconds per scan.

Calculations

The following formula is used to calculate the response factors of the internal standard to each of the calibration standards.

$$RF = (A_S C_{IS}) / (A_{IS} C_S)$$

where:

A_s = Area of the characteristic ion for the parameter to be measured.

A_{is} = Area of the characteristic ion for the internal standard.

C_{is} = Concentration of the internal standard, (ng/mL).

C_s = Concentration of the parameter to be measured, (ng/mL).

Based on these response factors, sample extract concentration for each PAH is calculated using the following formula.

$$C_e = \frac{(A_s)(I_s)}{(A_{is})(RF)}$$

where:

C_e = Sample extract concentration (ng/ml)

A_s = Area of the characteristic ion for the parameter to be measured.

A_{is} = Area of the characteristic ion for the internal standard.

I_s = Amount of internal standard added to each extract (ng/mL).

The actual sample concentration (C) for each compound is calculated by the following formula:

$$C = (C_e) \times \left(\frac{V_E}{V_s} \right),$$

where

C = Concentration in sample (ng/l)

V_E = The final extract volume (mL), and

V_s = The original volume of sample extracted (L).

8.3 Extended Analysis for Phenolics in GAC Plant

The analyst will select three appropriate internal standards. Calibration standards will be prepared for each parameter listed in Table 8-7 at three concentrations. A known constant amount of the three internal standards will be added to each standard mixture. The standard

TABLE 8-7
EXTENDED ANALYSES ACID EXTRACTABLES

4-chloro-3-methylphenol
2-chlorophenol
2,4-dichlorophenol
2,4-dimethylphenol
2,4-dinitrophenol
2-methyl-4,6-dinitrophenol
2-nitrophenol
4-nitrophenol
Pentachlorophenol
Phenol
2,4,6-trichlorophenol

mixtures will be analyzed according to Section 13 of EPA Method 625 (see Appendix B). Response factors (RF) will be calculated for each compound using the following formula:

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where

- A_s = Area of the characteristic m/z for the parameter to be measured.
- A_{is} = Area of the characteristic m/z for the internal standard.
- C_{is} = Concentration of the internal standard ($\mu\text{g/L}$).
- C_s = Concentration of the parameter to be measured ($\mu\text{g/L}$).

If the RF value over the working range is a constant (<35% relative standard deviation (RSD)), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} , vs. RF.

The working calibration curve or RF will be verified on each working day by the measurements of one or more calibration standards. If the response for any parameter varies from the predicted response by more than $\pm 20\%$, the test will be repeated using a fresh calibration standard. Alternatively, a new calibration curve will be prepared for that compound.

8.4 Expanded Analyses

Table 8-8 lists the parameters to be included in the expanded analyses with appropriate analytical method references. Detailed calibration procedures are included in each EPA method. Copies of these analytical methods are included in the appendices. Calibration for all parameters in the expanded analyses will be performed as set forth in the methods.

8.5 Non-Criteria PAH Analyses

Non-criteria water samples for PAH will be analyzed according to EPA Method 625 with the following changes. The compounds to be analyzed will be only those shown on Table 8-9 using the indicated internal standards and surrogates. ERT will prepare a five-point calibration curve as described in EPA 625 Section 7. The standard mixtures will be analyzed according to

TABLE 8-8
EXPANDED ANALYSES ANALYTE LIST AND
METHOD REFERENCE

<u>Analytes</u>	<u>Method Reference</u>
Volatile Organics	EPA 624 ¹
Acid, Base/Neutral Extractable Organics	EPA 625 ¹
Priority Pollutant Metals	EPA 200.7, 204.2, 206.2, 245.1, 270.2, 279.2 ²
Ammonia	EPA 350.2 ²
Chloride	EPA 325.2 ²
Sodium	EPA 200.7
Sulfate	EPA 375.4 ²
Total Phenol	420.1 ²
Cyanide	335.2 ²

¹ "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act" Federal Register, Friday, October 26, 1984.

² "Methods for Chemical Analysis of Water and Wastes" EPA-600/4-79-020, March 1979 (Revised March 1983).

TABLE 8-9
COMPOUNDS AND MS QUANTITATION MASS IONS

<u>Compound</u>	<u>Quantitation Mass Ion</u>	<u>Internal Standard Reference</u>
<u>Polynuclear Aromatic Hydrocarbons (PAH)</u>		
Naphthalene	128	1
Acenaphthylene	152	1
Acenaphthene	154	1
Fluorene	166	2
Phenanthrene	178	2
Anthracene	178	2
Fluoranthene	202	2
Pyrene	202	2
Benzo(a)anthracene	228	3
Chrysene	228	3
Benzofluoranthenes	252	3
Benzo(a)pyrene	252	3
Indeno(1,2,3,cd)pyrene	276	3
Dibenz(a,h)anthracene	278	3
Benzo(g,h,i)perylene	276	3
<u>Internal Standards</u>		
1) Acenaphthene-d10	164	-
2) Phenanthrene-d10	188	-
3) Benzo(a)pyrene-d12	264	-
<u>Surrogates</u>		
1) Naphthalene-d8	136	1
2) Fluorene-d10	176	2
3) Chrysene-d12	240	3

TABLE 8-9 (Continued)
COMPOUNDS AND MS QUANTITATION MASS IONS

<u>Compound</u>	<u>Quantitation Mass Ion</u>	<u>Internal Standard Reference</u>
<u>Heterocycles and Other PAH</u>		
Indene	116	1
Indole	117	1
2,3-dihydroindene	118	1
2,3-benzofuran	118	1
Quinoline	129	2
Benzo(b)thiophene	134	2
2-methyl naphthalene	141	2
1-methyl naphthalene	141	2
Biphenyl	154	3
Carbazole	167	3
Dibenzofuran	168	3
Acridine	179	3
Dibenzothiophene	184	3
Perylene	252	3
Benzo(e)pyrene	252	3
<hr/> <u>Internal Standards</u>		
1) Acenaphthene-d10	164	-
2) Phenanthrene-d10	188	-
3) Benzo(a)pyrene-d12	264	-
<hr/> <u>Surrogates</u>		
1) Naphthalene-d8	136	1
2) Flourene-d10	176	2
3) Chrysene-d12	240	3

Section 13 of EPA Method 625 (see Appendix B). Response factors (RF) will be calculated for each compound using the quantitation masses shown on Table 8-9 and the following formula:

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where

- A_s = Area of the characteristic m/z for the parameter to be measured.
- A_{is} = Area of the characteristic m/z for the internal standard.
- C_{is} = Concentration of the internal standard ($\mu\text{g/L}$).
- C_s = Concentration of the parameter to be measured ($\mu\text{g/L}$).

If the RF value over the working range is a constant (<35% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} , vs. RF.

The working calibration curve or RF will be verified on each working day by the measurements of one or more calibration standards. If the response for any parameter varies from the predicted response by more than $\pm 20\%$, the test will be repeated using a fresh calibration standard. Alternatively, a new calibration curve will be prepared for that compound.

9. ANALYTICAL PROCEDURES

9.1 Low Level Analysis of PAH and Heterocycles

9.1.1 Summary

This method has been designed for the analysis of PAH and heterocycles at the part per trillion level (ppt, ng/L) in water. The analysis is carried out by isolation of the target analytes by liquid-liquid extraction of the water sample with an organic solvent. Quantitation of the isolated target analytes is performed by gas chromatography mass spectrometry (GC/MS) in the selected ion monitoring mode (SIM). The compounds listed in Table 9-1 can be quantitatively determined using this analytical method.

Four 1-liter volumes of sample are separated into two 2-liter samples and extracted with methylene chloride. Analysis of the combined and concentrated extract is performed by gas chromatography/mass spectrometry using the selected ion monitoring scanning mode under electron impact ionization conditions.

9.1.2 Interferences

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks.

Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the environment being sampled.

9.1.3 Apparatus

Glassware

Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. This should be followed by detergent washing with hot water, and rinses with tap water, reagent water, then methanol. It should then be oven dried at 150°C for 30 minutes, and heated in a muffle furnace at 400°C for 15 to 30 minutes. Solvent rinses with methylene chloride may be substituted for the muffle furnace heating. Volumetric glassware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in

TABLE 9.1
COMPOUNDS AND MS QUANTITATION MASS IONS

Compound	Quantitation Mass Ion	Confirmation Ion (% Abundance)	Internal Standard Reference
<u>Polynuclear Aromatic Hydrocarbons (PAH)</u>			
Naphthalene	128	102 (20)	1
Acenaphthylene	152	151 (20)	1
Acenaphthene	154	153 (90)	1
Fluorene	166	165 (80)	2
Phenanthrene	178	176 (20)	2
Anthracene	178	176 (20)	2
Fluoranthene	202	200 (20)	2
Pyrene	202	200 (20)	2
Benzo(a)anthracene	228	226 (20)	3
Chrysene	228	226 (20)	3
Benzo(a)fluoranthene	252	250 (25)	3
Benzo(a)pyrene	252	250 (25)	3
Indeno(1,2,3-cd)pyrene	276	274 (20)	3
Dibenz(a,h)anthracene	278	276 (20)	3
Benzo(g,h,i)perylene	276	274 (20)	3
<u>Internal Standards</u>			
1) Acenaphthene-d10	164		-
2) Phenanthrene-d10	188		-
3) Benz(a)pyrene-d12	264		-
<u>Surrogates</u>			
1) Naphthalene-d8	136		1
2) Fluorene-d10	176		2
3) Chrysene-d12	240		3

TABLE 9.1 (Continued)
COMPOUNDS AND MS QUANTITATION MASS IONS

Compound	Quantitation Mass Ion	Confirmation Ion (% Abundance)	Internal Standard Reference
<u>Heterocycles and Other PAH</u>			
Indene	116	115 (90)	1
Indole	117	90 (40)	1
2,3-dihydroindene	118	117 (50)	1
2,3-benzofuran	118	90 (40)	1
Quinoline	129	102 (30)	2
Benzo(b)thiophene	134	-	2
2-methyl naphthalene	141	115 (40)	2
1-methyl naphthalene	141	115 (40)	2
Biphenyl	154	153 (30)	3
Carbazole	167	166 (25)	3
Dibenzofuran	168	139 (25)	3
Acridine	179	178 (25)	3
Dibenzothiophene	184	139 (20)	3
Perylene	252	250 (30)	3
Benzo(e)pyrene	252	250 (30)	3
<u>Internal Standards</u>			
1) Acenaphthene-d10	164	-	-
2) Phenanthrene-d10	188	-	-
3) Benz(a)pyrene-d12	264	-	-
<u>Surrogates</u>			
1) Naphthalene-d8	136	-	1
2) Flourene-d10	176	-	2
3) Chrysene-d12	240	-	3

a clean environment to prevent any accumulation of dust or other contaminants. Store it inverted or capped with aluminum foil. The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

- a) Separatory funnel - 3000 mL, with Teflon stopcock.
- b) Concentrator tube, Kuderna-Danish - 10 mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground-glass stopper is used to prevent evaporation of extracts.
- c) Snyder column, Kuderna-Danish - Three-ball macro (Kontes K-503000-0121 or equivalent).
- d) Evaporative flask, Kuderna-Danish - 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.
- e) Snyder column, Kuderna-Danish - two-ball micro (Kontes K-569001-0219 or equivalent).
- f) Micro reaction vessels, 2.0 mL (Supelco 3-3295).

Gas Chromatograph

The analytical system is complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port is designed for on-column injection when using packed columns and for splitless injection when using capillary columns.

Column

A J&W 15-meter fused silica capillary column coated with DB-5 bonded phase, or equivalent.

Mass Spectrometer

A mass spectrometer operating at 70 ev (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the ion abundance criteria when 50 ng of decafluorotriphenyl phosphine (DFTPP; bis(perfluorophenyl) phenyl phosphine) is injected through the GC inlet. The GC capillary column is fed directly into the ion source of the mass spectrometer.

A computer system interfaced to the mass spectrometer allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer has software that allows searching any GC/MS data file for ions of a specific mass and plotting such ion abundances versus time or scan number. The computer allows acquisition at pre-selected mass windows for selected ion monitoring.

Reagents

- a) Reagent water - Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each parameter of interest.
- b) Solvents - Acetone, methanol, methylene chloride, benzene, cyclohexane - Burdick & Jackson, distilled in glass, or equivalent.
- c) Sodium sulfate - (ACS) Granular, anhydrous. Purify by heating at 400°C for 4 hrs. in a shallow tray.
- d) Surrogate Spiking Solution - A solution containing 10 ng/mL of each of naphthalene-d₈, fluorene-d₁₀, and chrysene-d₁₂ (or equivalent weight deuterated PAH) is prepared by weighing appropriate aliquots of the purified crystals into a volumetric flask and dilution to volume with methanol or acetone.
- e) Internal Standard Solutions - A solution containing ca. 200 ng/mL of each internal standard is prepared by weighing an appropriate aliquot of each purified crystal into a volumetric flask and diluting to volume with methylene chloride. The internal standard compounds are acenaphthene-d₁₀, phenanthrene-d₁₀, and benzo(a)pyrene-d₁₂, or equivalent weight deuterated PAH, not used as a surrogate.
- f) Matrix Recovery Standard Spiking Solution - A solution containing the following compounds at the listed concentrations is prepared by weighing an appropriate aliquot of each purified crystal into a volumetric flask and diluting to volume with methanol or acetone.

<u>Compound</u>	<u>Concentration (ng/mL)</u>
Naphthalene	100
Fluorene	20
Chrysene	20
Benzo(g,h,i) perylene	20
Indene	20
Quinoline	20
Benz(e)pyrene	20
2-methylnaphthalene	20

9.1.4 Extraction

Samples

Samples are extracted at pH >12. Each 4-liter sample is separated into two 2-liter aliquots in two 3-liter separatory funnels. Each 2-liter aliquot is spiked in the separatory funnel with the surrogate spiking solution. A 2.00 mL volume of mixed surrogate spiking standard is added to each 3-liter separatory funnel, to give an approximate concentration of 10 ng/L (10 ppt) of each surrogate. Each aliquot is then extracted three times (80 mL/80 mL/80 mL) with methylene chloride. The three methylene chloride extracts are passed through an anhydrous sodium sulfate drying column, and combined in a Kuderna-Danish evaporative concentrator.

Concentrate the extract to approximately 0.5 mL and transfer to a 2.0 mL microreaction vessel containing 0.5 mL (500 μ l) of benzene. The methylene chloride is evaporated using a nitrogen stream. The evaporative concentrator tube is successively rinsed with methylene chloride, the rinsings added to the reaction vessel and the methylene chloride again evaporated. Continue this process until at least five (5) 1 mL rinsings of the tube have occurred. Evaporate the final methylene chloride, leaving the 500 μ l of benzene. All microreaction vessels should be permanently marked at the 500 μ l level and additional benzene added, when necessary, to insure a final 500 μ l extract volume. Cap with a Teflon fitted septum cap and store the extract at 4°C prior to GC/MS analysis.

Method Blank

For a minimum of 5% of the analyses performed, prepare a method blank by treating a 4-L sample of laboratory reagent water exactly as described above.

Solvent Blank

For a minimum of 10% of the analyses performed, prepare a solvent blank by introducing methylene chloride into two clean 3-liter separatory funnels (80 mL/80 mL/80 mL). Combine the methylene chloride extracts and continue the concentration exactly as described above.

Matrix Recovery Sample

For a minimum of 5% of the analyses performed, prepare a matrix recovery sample by spiking 2.00 mL of the matrix recovery standard spiking solution into two 2-L volumes of water collected from the GAC plant for ppt analyses and field collected for ppb analyses. Extract the fortified sample exactly as described above for samples. At this level of spiking, the following compounds will be introduced into the 4-L sample at the following concentrations:

<u>Compound</u>	<u>Concentration (ng/mL)</u>
Naphthalene	100
Fluorene	20
Chrysene	20
Benzo(g,h,i) perylene	20
Indene	20
Quinoline	20
Benz(e)pyrene	20
2-methylnaphthalene	20

Duplicate Sample

For a minimum of 10% of the samples analyzed a duplicate sample will be taken at sampling and a duplicate analysis will be performed. This will be carried out to insure that an estimate of precision will be available.

9.1.5 GC/MS Calibrations

Prior to use of method for low level analysis of PAH and Heterocycles, a five-point response factor calibration curve must be established showing the linear range of the analysis. For every 12 hours of GC/MS analysis, the mass spectrometer response for each PAH or heterocycle relative to the internal standard is determined, as described in the Calculations Section, using daily check standards at concentrations of 40 ng/mL. Daily response factors for each compound must be compared to the initial calibration curve. If the daily response factors are within ± 35 percent of the corresponding calibration curve value the analysis may proceed. If, for any

analyte, the daily response factor is not within ± 35 percent of the corresponding calibration curve value, a five-point calibration curve must be repeated for that compound prior to the analysis of samples.

Chromatographic peak location criteria will be established using relative retention time. An initial determination of retention times for each PAH or heterocycle relative to its respective internal standard (Table 9-1) will be made using the five-point calibration standards. Representative average relative retention times, standard deviations and 95 percent confidence limits are presented in Table 9-2. Relative retention times of daily check standards must be within the 95 percent confidence limits calculated from the calibration standards for each PAH or heterocyclic compound. In addition, sample component relative retention times must be within ± 0.1 relative retention time units of the standard component relative retention time.

9.1.6 Daily GC/MS Performance Tests

At the beginning of each 12 hour shift that analyses are to be performed, the GC/MS system must be checked to see that acceptable performance criteria are achieved for DFTPP. This DFTPP performance test requires the following instrumental parameters:

Electron Energy 70 volts (nominal)
Mass Range - 35 to 450 amu
Scan Time - 1.0 sec.

At the beginning of each 12 hour shift, inject 2 μL (50 ng) of DFTPP standard solution. Obtain a background corrected mass spectrum of DFTPP and check that all the key ion criteria in Table 9-3 are reasonably achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved.

9.1.7 Gas Chromatography/Mass Spectrometry Analysis

Just prior to analysis a 125 μL aliquot of internal standard solution is transferred to the sample vial using a 250 μL syringe, giving a final internal standard concentration of ca. 40 ng/mL in the extract. Representative aliquots are injected into the capillary column of the gas chromatograph using the following, or similar, conditions:

Injector Temp - 290°C
Transfer Line Temp - 310°C
Initial Oven Temp - 35°C
Initial Hold Time - 2 min.
Ramp Rate - 10°C/min.
Final Temperature - 310°C

TABLE 9-2

RELATIVE RETENTION TIMES AND CONFIDENCE LIMITS FOR THE COMPOUNDS
ASSOCIATED WITH THE LOW LEVEL PAH AND HETEROCYCLE METHODOLOGY

<u>Group 1</u>	<u>Avg. RRT</u>	<u>SD</u>	<u>% RSD</u>	<u>95% Confidence Limits</u>
benzofuran	0.550	0.015	2.807	0.520-0.580
dihydroindene	0.590	0.016	2.765	0.558-0.622
indene	0.598	0.016	2.699	0.566-0.630
Naphthalene-d8 (Surr.)	0.733	0.017	2.289	0.699-0.767
Naphthalene	0.735	0.017	2.289	0.701-0.769
Benz(b)thiophene	0.743	0.017	2.258	0.709-0.777
Quinoline	0.783	0.017	2.140	0.749-0.817
Indole	0.824	0.018	2.167	0.788-0.860
2-methyl	0.832	0.017	2.084	0.798-0.866
1-methyl	0.848	0.017	2.055	0.814-0.882
Biphenyl	0.901	0.017	1.921	0.867-0.935
Acenaphthylene	0.962	0.018	1.822	0.927-0.988
Acenaphthene	0.988	0.018	1.849	0.952-1.024
Dibenzofuran	1.011	0.018	1.791	0.975-1.047
 Group II				
Fluorene-d10 (Surr.)	0.872	0.015	1.735	0.842-0.902
Fluorene	0.875	0.015	1.745	0.845-0.905
Dibenzothiophene	0.974	0.016	1.617	0.942-1.006
Phenanthrene	0.988	0.016	1.589	0.956-1.020
Anthracene	0.994	0.016	1.597	0.962-1.026
Acridine	0.999	0.016	1.572	0.967-1.031
Carbazole	1.013	0.015	1.487	0.983-1.043
Fluoranthene	1.130	0.017	1.461	1.096-1.164
Pyrene-d10 (Surr.)	1.155	0.017	1.444	1.121-1.189
Pyrene	1.157	0.017	1.443	1.123-1.191
 Group III				
Benz(a)anthracene	0.873	0.012	1.325	0.849-0.897
Chrysene-d12 (Surr.)	0.874	0.012	1.320	0.850-0.898
Chrysene	0.876	0.012	1.320	0.852-0.900
Benzofluoranthenes	0.960	0.014	1.501	0.932-0.988
Benzo(e)pyrene	0.984	0.016	1.590	0.952-1.016
Benzo(a)pyrene	0.988	0.016	1.615	0.956-1.020
Perylene-d12 (Surr.)	0.944	0.016	1.634	0.962-1.026
Perylene	0.996	0.016	1.644	0.964-1.028
Indeno (123,cd)pyrene	1.114	0.025	2.276	1.064-1.164
Dibenz(ah)anthracene	1.113	0.031	2.743	1.051-1.175
Benzo(ghi)perylene	1.149	0.028	2.422	1.093-1.205

TABLE 9-3

DFTPP ION ABUNDANCE CRITERIA

<u>Mass</u>	<u>Ion Abundance Criteria</u>
51	30 to 60 percent of mass 198
68	less than 2 percent of mass 69
70	less than 2 percent of mass 69
127	40 to 60 percent of mass 198
197	less than 1 percent of mass 198
198	base peak, 100 percent
199	5 to 9 percent of mass 198
275	10 to 30 percent of mass 198
365	greater than 1 percent of mass 198
441	present but less than mass 443
442	greater than 40 percent of mass 198
443	17 to 23 percent of mass 442

The effluent from the GC capillary column is fed directly into the ion source of the mass spectrometer. The MS is operated in the selected ion monitoring (SIM) mode using appropriate windows to include the quantitation and confirmation masses of each PAH or heterocycle as shown in Table 9-1. The time programmed SIM acquisition windows are listed in Table 9-4. Each SIM sequence is acquired at a total scan speed of 1.1 seconds per scan. Typical retention behavior of the combined PAH and heterocycle analytes and corresponding SIM sequences are shown in Table 9-5. For all compounds detected at a concentration above the MDL, a check is made to insure the confirmation ion is present.

9.1.8 Calculations

The following formula is used to calculate the response factors of the internal standard to each of the calibration standards.

$$RF = (A_s C_{is}) / (A_{is} C_s)$$

where:

A_s = Area of the characteristic ion for the parameter to be measured.

A_{is} = Area of the characteristic ion for the internal standard.

C_{is} = Concentration of the internal standard, (ng/mL).

C_s = Concentration of the parameter to be measured, (ng/mL).

Based on these response factors, sample extract concentration for each PAH is calculated using the following formula.

$$C_e = \frac{(A_s)(I_s)}{(A_{is})(RF)}$$

where:

C_e = Sample extract concentration (ng/mL)

A_s = Area of the characteristic ion for the parameter to be measured.

A_{is} = Area of the characteristic ion for the internal standard.

I_s = Amount of internal standard added to each extract (ng/mL).

The actual sample concentration (C) for each compound is calculated by the following formula:

TABLE 9-4
SELECTED ION MONITORING (SIM) SEQUENCE FOR
PAH AND HETEROOCYCLES

<u>Sequence #</u>	<u>M/Z Scanned</u>	<u>Scan # Range</u>	<u>Start Time (Min)</u>
1	90, 115, 116, 117, 118	300-499	5.50
2	102, 128, 129, 134, 136	500-599	9.17
3	90, 115, 117, 141, 153, 154	600-719	11.00
4	139, 151, 152, 153, 154, 164, 165, 166, 168, 176	720-899	13.20
5	139, 166, 167, 176, 178, 179, 184, 188	900-1049	16.50
6	200, 202, 212	1050-1249	19.25
7	226, 228, 240	1250-1399	22.92
8	250, 252, 264	1400-1649	25.67
9	274, 276, 278	1650-1850	30.25

TABLE 9-5
GC RETENTION BEHAVIOR FOR PAH AND HETEROCYCLES

<u>Compound</u>	<u>M/Z</u>	Retention	
		<u>Scan</u> <u>Number</u>	<u>SIM</u> <u>Sequence #</u>
2,3-benzofuran	118	383	1
2,3-dihydroindene	118	420	1
Indene	116	429	1
Napthalene-d8 (Surr.)	136	548	2
Napthalene	128	551	2
Benzo(b)thiophene	134	557	2
Quinoline	129	593	2
Indole	117	635	3
2-methylnapthalene	141	640	3
1-methylnapthalene	141	653	3
Biphenyl	154	703	3
Acenaphthylene	152	756	4
Acenaphthene-d10 (IS-1)	164	776	4
Acenaphthene	154	781	4
Dibenzofuran	168	802	4
Fluorene-d10 (Surr.)	176	843	4
Fluorene	166	848	4
Dibenzothiophene	184	956	5
Phenanthrene-d10 (IS-2)	188	970	5
Phenanthrene	178	974	5
Anthracene	178	980	5
Acridine	179	985	5
Carbazole	167	1004	5
Fluoranthene	202	1134	6
Pyrene	202	1162	6
Benz(a)anthracene	228	1333	7
Chrysene-d12 (Surr.)	240	1335	7
Chrysene	228	1339	7
Benzofluoranthenes	252	1496	8
Benz(e)pyrene	252	1536	8
Benz(a)pyrene-d12 (IS-3)	264	1539	8
Benz(a)pyrene	252	1543	8
Perylene	252	1546	8
Indeno (1,2,3-cd)pyrene	276	1713	9
Dibenz(a,h)Anthracene	278	1718	9
Benzo(g,h,i)Perylene	276	1750	9

$$C = (C_e) \times \left(\frac{V_E}{V_S} \right),$$

where

C = Concentration in Sample (ng/L)

V_E = The final extract volume (mL), and

V_S = The original volume of sample extracted (L).

9.2 Extended Analyses for Carcinogenic PAH in GAC Plant

To satisfy the requirements of the RAP Section 4.3.4, ERT will analyze one sample per year of the GAC treated water for the additional carcinogenic compounds shown on Table 9-6 and search for additional compounds that may be present. ERT will first analyze the sample according to Section 9.1 of this QAPP. A calibration standard containing the compounds shown on Table 9-6 will be prepared and used to establish a five point calibration curve. All procedures outlined in Section 8.2 for instrument calibration will be followed.

The sample extract will be prepared and analyzed as outlined in Section 9.1 generating quantitative results for the compounds being regularly measured. A second injection will be made with a selective ion monitoring program using the quantitation masses shown in Table 9-6. This will allow the extended analysis compounds to be quantitated at an approximately 2 ppt detection limit.

Following the quantitative analyses of the regular and extended analysis compounds, the extract will be reduced to a 50 ul final volume. An aliquot will be analyzed using full-scan GC/MS (40-500 amu). Any peaks having a signal to noise ratio of 5 or larger will be identified, if possible, using the EPA/NIH mass spectral library. Compounds so identified will be quantitated using the nearest internal standard and a response factor of 1.0, to a detection limit of approximately 5 ppt.

9.3 Extended Analyses for Phenolics in GAC Plant

To satisfy the requirements of the RAP Section 4.3.4, ERT will analyze one sample per year of GAC treated water for the acid extractable compounds shown on Table 9-7. These compounds will be analyzed according to sections applicable to acid extractables in EPA Method 625 ("Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act". Federal Register, Friday, October 26, 1984).

9.4 Expanded Analyses

In accordance with RAP Section 9.3.3, the Regional Administrator, the Director, or the Commissioner may request expanded analyses of groundwater

TABLE 9-6
EXTENDED ANALYSIS CARCINOGENIC PAH

<u>Compound</u>	<u>Quantitation Mass</u>
benzo(c)phenanthrene	226
dibenz(a,c)anthracene	278
dibenz(a,e)pyrene	276
dibenz(a,h)pyrene	276
dibenz(a,i)pyrene	276
7,12-dimethylbenz(a)anthracene	256
3-methylcholanthrene	268

TABLE 9-7
EXTENDED ANALYSES ACID EXTRACTABLES

4-chloro-3-methylphenol
2-chlorophenol
2,4-dichlorophenol
2,4-dimethylphenol
2,4-dinitrophenol
2-methyl-4,6-dinitrophenol
2-nitrophenol
4-nitrophenol
Pentachlorophenol
Phenol
2,4,6-trichlorophenol

samples in conjunction with the Northern Area Remedial Investigation. The list of possible analyses are shown on Table 9-8. Organic analyses and metals analyses will be performed at ERT's Concord laboratory facility. The inorganic analyses will be performed at ERT's Houston laboratory facility.

The analytical methods to be used for each analyte are also shown on Table 9-8 and attached as Appendix B.

9.5 Non-Criteria PAH Analyses

Non-criteria PAH samples will be analyzed, according to EPA Method 625 (see Appendix B) with the following exceptions:

- 1) The compounds analyzed list will be limited to those compounds listed in QAPP Table 9-9.
- 2) Deuterated PAH will be used for surrogates and internal standards, as shown on Table 9-9.
- 3) Matrix spikes will be analyzed as detailed in QAPP Section 11.1.4 using the select list of matrix spike compounds as shown therein.
- 4) Surrogate and matrix spike acceptance criteria will be those given in QAPP Section 15.1.

As described in EPA 625, a one-liter water sample will be extracted and analyzed, to give a reported detection limit of 10 parts per billion for each compound.

TABLE 9-8
EXPANDED ANALYSES ANALYTE LIST AND
METHOD REFERENCE

<u>Analytes</u>	<u>Method Reference</u>
Volatile Organics	EPA 624 ¹
Acid, Base/Neutral Extractable Organics	EPA 625 ¹
Priority Pollutant Metals	EPA 200.7, 204.2, 206.2, 245.1, 270.2, 279.2 ²
Ammonia	EPA 350 ²
Chloride	EPA 325 ²
Sodium	EPA 200.7 ²
Sulfate	EPA 375 ²

¹ "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act" Federal Register, Friday, October 26, 1984.

² "Methods for Chemical Analysis of Water and Wastes" EPA-600/4-79-020, March 1979.

TABLE 9-9
COMPOUNDS AND MS QUANTITATION MASS IONS

<u>Compound</u>	<u>Quantitation Mass Ion</u>	<u>Internal Standard Reference</u>
<u>Polynuclear Aromatic Hydrocarbons (PAH)</u>		
Naphthalene	128	1
Acenaphthylene	152	1
Acenaphthene	154	1
Fluorene	166	2
Phenanthrene	178	2
Anthracene	178	2
Fluoranthene	202	2
Pyrene	202	2
Benzo(a)anthracene	228	3
Chrysene	228	3
Benzofluoranthenes	252	3
Benzo(a)pyrene	252	3
Indeno(1,2,3,cd)pyrene	276	3
Dibenz(a,h)anthracene	278	3
Benzo(g,h,i)perylene	276	3
<hr/>		
Internal Standards		
1) Acenaphthene-d10	164	-
2) Phenanthrene-d10	188	-
3) Benzo(a)pyrene-d12	264	-
<hr/>		
Surrogates		
1) Naphthalene-d8	136	1
2) Fluorene-d10	176	2
3) Chrysene-d12	240	3

TABLE 9-9 (Continued)
COMPOUNDS AND MS QUANTITATION MASS IONS

<u>Compound</u>	<u>Quantitation Mass Ion</u>	<u>Internal Standard Reference</u>
<u>Heterocycles and Other PAH</u>		
Indene	116	1
Indole	117	1
2,3-dihydroindene	118	1
2,3-benzofuran	118	1
Quinoline	129	2
Benzo(b)thiophene	134	2
2-methyl naphthalene	141	2
1-methyl naphthalene	141	2
Biphenyl	154	3
Carbazole	167	3
Dibenzofuran	168	3
Acridine	179	3
Dibenzothiophene	184	3
Perylene	252	3
Benzo(e)pyrene	252	3
<u>Internal Standards</u>		
1) Acenaphthene-d10	164	-
2) Phenanthrene-d10	188	-
3) Benzo(a)pyrene-d12	264	-
<u>Surrogates</u>		
1) Naphthalene-d8	136	1
2) Flourene-d10	176	2
3) Chrysene-d12	240	3

10. DATA REDUCTION, VALIDATION AND REPORTING

10.1 Data Reduction and Validation

All data will be subjected to a rigorous review process before being reported. All data forms must be dated, signed and completely filled out in ink by the preparer. Notes will be made if information requested is non-applicable for the specific analysis. Each data sheet will be checked, signed, dated and approved by someone other than the preparer.

Out-of-control events or potential out-of-control events are noted on an out-of-control event form. This form is part of the data package and will be completed upon data approval. If no out-of-control events are encountered then this will also be documented. If an out-of-control event does occur during analysis, for instance a surrogate recovery falls outside the expected range, the analyst will describe the event, the investigative and corrective action taken and the cause of the event on this form, and will notify the Quality Control Coordinator (QCC).

After an analyst completes a Data Package, it is given to the Supervisor for review. The Supervisor reviews the entire Data Package for completeness, discrepancies and errors and writes comments, when necessary, on the back of the Data Approval Form. If the supervisor disapproves the Data Package it is given back to the analyst for correction. If it is approved the Supervisor passes it along to the QCC.

The QCC then reviews the Data Package with extra emphasis on the acceptability of quality control data. If the QCC disapproves the Data Package it is rerouted to the Supervisor for corrective action; if the QCC approves it, it is sent to the Laboratory Manager for final approval and report preparation.

Before submission to the client, the final typed report is reviewed by the Program Manager, Laboratory Manager, Supervisors and Quality Control Coordinator for their approval and signatures.

10.2 Turnaround Time

In accordance with Section 3.2 of the RAP, ERT has agreed to a 28-day turnaround. The City, however, makes no enforceable commitment under the RAP except for a maximum of 7 days for extraction of organics and 40 days following extraction for analysis of organics. For non-organic analyses, the City makes no enforceable commitment under the RAP except to meet the recommended maximum analytical holding times.

10.3 Report Descriptions

10.3.1 Method Detection Limit Report

The Method Detection Limit Report will consist of a tabulation of method detection limits (MDL) and lower confidence limits (LCL) for each compound analyzed. These concentration limits will be utilized in completing the Analytical Results Report (10.3.2) for all samples analyzed. An example of this report is included as Figure 10-1.

FIGURE 10-1
ERT ANALYTICAL LABORATORY METHOD DETECTION LIMITS
POLYAROMATIC HYDROCARBONS

<u>Compound</u>	<u>Method Detection Limit (MDL)</u>	<u>Lower Control Limit (LCL)</u>
Naphthalene	47	30
Acenaphthylene	1.7	1.1
Acenaphthene	1.3	0.83
Fluorene	0.88	0.56
Phenanthrene	3.1	2.0
Anthracene	3.4	2.2
Fluoranthene	4.4	2.8
Pyrene	4.1	2.6
Benz(a)anthracene	4.4	2.8
Chrysene	4.4	2.8
Benzofluoranthenes	9.7	6.2
Benzo(a)pyrene	3.4	2.2
Indeno(1,2,3,cd)pyrene	4.4	2.8
Dibenz(a,h)anthracene	3.4	2.2
Dibenzo(g,h,i)perylene	5.3	3.4
Indene	2.9	1.8
Indole	1.9	1.2
2,3-dihydroindene	3.4	2.2
2,3-benzofuran	1.9	1.2
Quinoline	1.9	1.2
Benzo(b)thiophene	2.2	1.4
2-methylnaphthalene	5.0	3.2
1-methylnaphthalene	3.1	2.0
Biphenyl	17	11
Carbazole	2.6	1.7
Dibenzofuran	1.2	0.77
Acridine	2.5	1.6
Dibenzothiophene	6.3	4.0
Perylene	1.6	1.0
Benzo(e)pyrene	1.5	0.96

All values expressed in part per trillion (ppt)

QUALITY ASSURANCE PROJECT PLAN

Page: 93 of 125
Date: Jan. 1987
Number: QA E415
Revision: 0

FIGURE 10-2 ERT ANALYTICAL LABORATORY SUMMARY OF ANALYTICAL RESULTS POLYAROMATIC HYDROCARBONS

Field ID: W-02

ERT No: 37015

CARCINOGENIC PAHs

<u>Parameters</u>	<u>Analytical Result</u> <u>(ng/l)</u>
Quinoline	ND
Benzo(a)anthracene	ND
Chrysene	ND
Benzofluoranthenes	ND
Benzo(a)pyrene	ND
Indeno(1,2,3-CD)pyrene	ND
Dibenzo(a,h)anthracene	ND
Benzo(g,h,i)perylene	ND
Total Carcinogenic PAH	ND

OTHER PAHs

2,3-benzofuran	ND
2,3-dihydroindene	7.7
indene	ND
Naphthalene	ND
Benzo(b)thiophene	ND
Indole	ND
2-methylnaphthalene	ND
1-methylnaphthalene	ND
Biphenyl	ND
Acenaphthylene	7.5
Acenaphthene	11
Dibenzofuran	<1.2
Fluorene	4.5
Dibenzothiophene	ND
Anthracene	<3.4
Acridine	ND
Carbazole	ND
Fluoranthene	ND
Pyrene	4.5
Benzo(e)pyrene	ND
Perylene	ND
Total Other PAH:	35
Total PAHs:	35

ND = Concentration <LCL of MDL
<MDL = Concentration >LCL but <MDL

FIGURE 10-3

ERT ANALYTICAL LABORATORY SUMMARY OF ANALYTICAL RESULTS
SURROGATE RECOVERY REPORT
POLYAROMATIC HYDROCARBONS

Field Id: W-02

ERT No: 37015

<u>Surrogate</u>	Spike Level (ppb)	Recovery %
Naphthalene - D8	9.9	35
Fluorene - D10	9.5	103
Chrysene - D12	9.8	80

FIGURE 10-4
ERT ANALYTICAL MATRIX SPIKE RECOVERY REPORT

Field Id: MS-02

ERT No: 37018

<u>Parameters</u>	<u>Spike Level</u> <u>(ng/l)</u>	<u>Observed</u> <u>(ng/l)</u>	<u>Recovery</u> <u>%</u>
Naphthalene	110	53.9	49
Fluorene	20.1	8.7	43
Chrysene	24.2	14.5	60
Benzo(g,h,i)perylene	22.4	2.02	9
Indene	24.6	6.88	28
Quinoline	23.5	12.2	52
Benzo(e)pyrene	20.4	2.45	12
2-methylnaphthalene	21.2	10.6	<u>50</u>
Average % Recovery:			38

QUALITY ASSURANCE PROJECT PLAN

Page: 96 of 125

Date: Jan. 1987

Number: QA E415

Revision: 0

<u>Parameter</u>	<u>Advisory Level</u>	<u>Drinking Water Criterion</u>
Sum of Benzo(a)pyrene and Dibenz(a,h)anthracene*	3.0 ng/L	5.6 ng/L
Total Carcinogenic PAH	15 ng/L**	28 ng/L**
Total Other PAH	175 ng/L	280 ng/L

*Or the detection limit, whichever is largest.

**Different concentrations for additional carcinogenic PAH may be established in accordance with the procedure specified in Part D.1 of the Consent Decree.

11. INTERNAL QUALITY CONTROL CHECK

11.1 Low-level PAH Analyses/Extended Analyses/Non-Criteria PAH Analyses

11.1.1 Method Detection Limit

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero. This is determined from duplicate analyses of a sample of a given matrix containing the analyte near the estimated detection limit.

ERT has determined the method detection limits for the part per trillion PAH analysis of water samples, utilizing GC/MS selected ion monitoring, as per the method described in Appendix B to Part 136 of the Friday, October 26, 1984 Federal Register, Vol. 49, No. 209 - Definition and Procedure for the Determination of the Method Detection Limit - Revision 11.1. Table 11-1 lists the compounds, the mean observed concentration of seven replicates spiked at 5 parts per trillion, the standard deviation, the method detection limit and the lower control limit (defined as 0.64 MDL).

These calculated method detection limits will be used in sample reporting as follows:

- Concentrations of samples (after blank correction, if applicable) less than the lower control limit of the method detection limit will be reported as not detectable (ND).
- Concentrations of samples (after blank correction, if applicable) greater than or equal to the lower control limit of the method detection limit, but less than the method detection limit will be reported as less than the MDL, or BDL (below detection limit).

11.1.2 Method Blank and Solvent Blank

The laboratory will analyze 10% laboratory solvent blanks and 5% method blanks as described in Section 9.0, Analytical Method.

The method blank results associated with the sample batch will be used to correct the observed sample concentrations in that batch as indicated below:

- If the concentration in the blank is less than or equal to half of the method detection limit, samples will not be corrected for the blank.
- If the concentration in the blank is greater than half of the method detection limit and is less than or equal to half the concentration detected in the sample, samples will be corrected for the blank by subtracting the value observed for the compound in the blank from the value observed for the same compound in the sample.

TABLE 11-1

METHOD DETECTION LIMIT STUDY

GC/MS/SIM PART PER TRILLION PAH/HETEROCYCLES IN WATER

<u>Compound</u>	<u>Mean</u>	<u>Standard Deviation</u>	<u>MDL</u>	<u>Lower Control Limit</u>
Naphthalene	29	15	47	30
Acenaphthylene	3.1	0.53	1.7	1.1
Acenaphthene	2.9	0.42	1.3	0.83
Fluorene	4.3	0.28	0.88	0.56
Phenanthrene	5.2	1.0	3.1	2.0
Anthracene	3.8	1.1	3.4	2.2
Fluoranthene	7.8	1.4	4.4	2.8
Pyrene	7.7	1.3	4.1	2.6
Benz(a)anthracene	7.4	1.4	4.4	2.8
Chrysene	7.6	1.4	4.4	2.8
Benzofluoranthenes	13	3.1	9.7	6.2
Benzo(a)pyrene	5.6	1.1	3.4	2.2
Indeno(1,2,3,cd)pyrene	7.9	1.4	4.4	2.8
Dibenz(a,h)anthracene	5.5	1.1	3.4	2.2
Dibenzo(g,h,i)perylene	6.3	1.7	5.3	3.4
Indene	3.3	0.92	2.9	1.8
Indole	4.2	0.61	1.9	1.2
2,3-dihydroindene	3.7	1.1	3.4	2.2
2,3-benzofuran	2.8	0.61	1.9	1.2
Quinoline	4.5	0.61	1.9	1.2
Benzo(b)thiophene	4.6	0.71	2.2	1.4
2-methylnaphthalene	6.6	1.6	5.0	3.2
1-methylnaphthalene	4.9	0.98	3.1	2.0
Biphenyl	14	5.4	17	11
Carbazole	5.4	0.84	2.6	1.7
Dibenzofuran	4.7	0.38	1.2	0.77
Acridine	3.6	0.81	2.5	1.6
Dibenzothiophene	4.6	2.0	6.3	4.0
Perylene	3.5	0.52	1.6	1.0
Benzo(e)pyrene	4.8	0.49	1.5	0.96

All values expressed in part per trillion (ppt)

- If the concentration in the blank is greater than half the method detection limit and is greater than half the concentration detected in the sample, correction is not possible and the compound in the sample should be reported as not applicable (NA). If this situation occurs, the cause of the high blank must be determined and corrective actions taken.

The solvent blank is not used to correct sample concentrations, but to help determine the cause of contamination in high blanks.

11.1.3 Surrogates

The laboratory will spike all samples and quality control samples with deuterated PAH surrogate compounds. The surrogate compounds will be spiked into the sample prior to extraction and, thus, will measure individual sample matrix effects associated with sample preparation and analysis. They will include naphthalene-d₈, fluorene-d₁₀ and chrysene-d₁₂, at a sample concentration level of 10 ng/L (ppt) or 20 µg/L (ppb). ERT will calculate the percent recovery of each surrogate for each sample. Prior to beginning work on the project ERT will calculate the 95% confidence limits for each surrogate using historical data. ERT will plot control charts for each surrogate with warning limits at two standard deviations. The control charts will be updated as sample surrogate recoveries are plotted, as a means of observing trends or changes in method precision. Control charts will be used to alert ERT to the need to check method procedures, but failure of a surrogate to fall within the 95% confidence limits of the ongoing control charts does not necessarily invalidate the sample data.

A sample will be invalid for quantitative use in this program only if the recovery of any one or more of the surrogates falls outside the acceptance criteria. The acceptance criteria used for this program are the criteria established by ERT for these surrogates during 1986. ERT will take corrective action whenever the surrogate recovery for any one or more surrogates is outside the following acceptance criteria:

<u>Surrogate</u>	<u>Acceptance Criteria %</u>	
	<u>Low-level</u>	<u>Non-criteria</u>
Naphthalene-d ₈	14-108	25-175
Fluorene-d ₁₀	41-162	25-175
Chrysene-d ₁₂	10-118	25-175

The following corrective action will be taken when required as stated above:

- a) Check calculations to assure there are no errors;
- b) Check internal standard and surrogate solutions for degradation, contamination, etc., and check instrument performance;
- c) Reanalyze the sample or extract if the steps in part a) or b) fail to reveal a problem. If reanalysis of the extracts yields surrogate spike recoveries within the stated limits, then the reanalysis data will be used. Both the original and reanalysis data will be reported.
- d) If a), b) or c) do not correct the problem, the data for that sample will be reported but will not count towards satisfying the monitoring requirements of the RAP.

11.1.4 Matrix Spikes

The laboratory will spike and analyze 5% matrix spike samples. Following the Contract Laboratory Program rationale, ERT will spike eight representative compounds into water from the GAC plant for ppt analyses and field collected for ppb analyses. These compounds and the spiking levels are listed below:

	<u>PPT</u>	<u>PPB</u>
Naphthalene	100 ng/L	50µg/L
Fluorene	20	50
Chrysene	20	50
Benzo(g,h,i)perylene	20	50
Indene	20	50
Quinoline	20	50
Benz(e)pyrene	20	50
2-methyl naphthalene	20	50

Naphthalene is spiked at a higher level in the ppt method, because of the higher method detection limit. The spiking procedure is outlined in Section 9.0 of this QAPP.

ERT will validate the analytical data by utilizing the matrix spike sample criteria in conjunction with the surrogate recovery criteria. If the criteria for the matrix spike are met, only samples which do not meet the surrogate recovery criteria in that batch will be considered invalid. If the matrix spike criteria are not met, the matrix spike analysis will be repeated. If the subsequent matrix spike analysis meets the criteria, the data will be considered valid.

The matrix spike criteria for data validity are as follows:

- The average of the percent recoveries for all eight compounds must fall between 20 and 150 percent.
- Only one compound can be below its required minimum percent recovery. These minimum percent recoveries are:
 - 1) 10% for chrysene, benzo(g,h,i)perylene, and benz(e)pyrene, and
 - 2) 20% for all other compounds.

Both matrix spike and surrogate spike recoveries will be used in assessing quality assurance/quality control for ERT's analytical work.

11.1.5 Duplicates

The laboratory will analyze 10% duplicate samples. Percent difference between duplicates will be calculated for each detected compound. The results will be plotted onto control charts and mean and standard deviation will be calculated.

11.2 Extended Analyses for Phenolics in GAC Plant

The laboratory will, on an ongoing basis, spike at least 5% of the samples to assess accuracy. For 1 to 20 samples per month, at least one spiked sample per month is required.

The concentration of the spike in the sample will be 100 µg/L. The percent recovery for each parameter will be compared with the corresponding QC acceptance criteria shown in Table 11-2. If any individual recovery falls outside the designated ranges, that parameter has failed the criteria.

If any parameter fails the acceptance criteria for recovery, a QC check standard containing each parameter that failed must be prepared and analyzed. The QC check sample will be prepared at a concentration of 100 µg/L for each parameter which failed in deionized water. The QC check sample will be analyzed and the percent recovery for each parameter calculated.

The percent recovery for each parameter in the QC check sample will be compared to the acceptance criteria in Table 11-2. If the recovery of any parameter falls outside the designated range, the analytical result for that parameter in the original unspiked samples is suspect and will not be used.

TABLE 11-2
ACCEPTANCE CRITERIA - EXTENDED ANALYSES FOR PHENOLICS¹

<u>Parameter</u>	<u>Acceptance Criteria</u> <u>(%)</u>
4-chloro-3-methylphenol	22-147
2-chlorophenol	23-134
2,4-dichlorophenol	39-135
2,4-dimethylphenol	32-119
2,4-dinitrophenol	D-191
2-methyl-4,6-dinitrophenol	D-181
2-nitrophenol	29-182
4-nitrophenol	D-132
Pentachlorophenol	14-176
Phenol	5-112
2,4,6-trichlorophenol	37-144

D = Detected; result must be greater than zero.

¹Reprinted from Table 6, page 43392 of "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act", Federal Register, Friday, October 26, 1984.

The laboratory will also spike all samples with a minimum of three surrogate compounds and calculate the percent recoveries. On-going quality control charts plotting surrogate percent recoveries will be prepared. The control charts will be updated as sample surrogate recoveries are plotted, as a means of observing trends or changes in method precision. Control charts will be used to alert ERT to the need to check method procedures, but failure of a surrogate to fall within the 95% confidence limits of the ongoing control charts does not necessarily invalidate the sample data.

11.3 Expanded Analyses

The Expanded Analyses required in this program will be carried out with the associated internal quality control program as summarized in Table 11-3. The quality control checks encompass the use of method blanks, field blanks, matrix spikes, and duplicates for all the analyses conducted. In addition, the GC/MS based methods for Volatile Organics (EPA 624) and Acid/Base/Neutral Extractable Organics (EPA 625) will be conducted by spiking multiple surrogate recovery compounds in all samples. Specific details to be followed for each analysis are contained in the appropriate Method Reference, all of which have been included in Appendix B.

QUALITY ASSURANCE PROJECT PLAN

Page: 104 of 125
Date: Jan. 1987
Number: QA E415
Revision: 0

TABLE 11-3
EXPANDED ANALYSES INTERNAL
QUALITY CONTROL CHECKS

<u>Analytes</u>	<u>Method Reference</u>	<u>QA/QC</u>				
		<u>Recovery</u> <u>Surrogates</u>	<u>Matrix</u> <u>Spike</u>	<u>Method</u> <u>Blank</u>	<u>Duplicate</u>	<u>Field</u> <u>Blank</u>
Volatile Organics	EPA 624 ¹	X ³	X	X	X	X
Acid, Base/Neutral Extractable Organics	EPA 625 ¹	X ⁴	X	X	X	X
Priority Pollutant Metals	EPA 200.7, 204.2, 206.2, 245.1, 270.2, 279.2 ²		X	X	X	X
Ammonia	EPA 350.2 ²		X	X	X	X
Chloride	EPA 325.2 ²		X	X	X	X
Sodium	EPA 200.7 ²		X	X	X	X
Sulfate	EPA 375.4 ²		X	X	X	X
Total Phenol	335.2 ²		X	X	X	X
Cyanide	335.2 ²		X	X	X	X

¹ "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act"
Federal Register, Friday, October 26, 1984.

² "Methods for Chemical Analysis of Water and Wastes" EPA-600/4-79-020, March 1979 (Revised March 1983).

³ 1,2-dichloroethane-d₄, benzene-d₆, toluene-d₈, and 4-bromo fluorobenzene spiked at 50 µg/L.

⁴ phenol-d₅, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d₅, 2-fluorobiphenyl, and benzo(a)pyrene-d₁₂ spiked at 100 µg/L in all samples.

12. PERFORMANCE AND SYSTEM AUDITS

ERT's Concord Analytical Chemistry Laboratory participates in a variety of interlaboratory testing and performance checks to provide periodic assessment of the effectiveness of the overall quality control program.

12.1 Interlaboratory Performance Surveys

Performance surveys conducted by the EPA and the Massachusetts Department of Environmental Quality Engineering (DEQE) constitute the bulk of interlaboratory comparisons.

- DEQE Performance Evaluations - Water Supply - Semiannual (May and November)
 - Trace Metals
 - Pesticides
 - Herbicides
 - THMs
 - Residual Free Chlorine
 - Turbidity
 - Total Filterable Residue
 - Calcium (as CaCO_3)
 - Alkalinity
 - pH
 - Corrosivity (@ 20°C)
 - Sodium
- EPA Performance Evaluations - Water Pollution - Semiannual (April and October)
 - Trace Metals
 - Minerals
 - Nutrients
 - Orthophosphate
 - Demands
 - Organics
 - Total Cyanide
 - Oil and Grease

ERT's performance is evaluated by the respective agency after each round of testing, and reported to ERT's Laboratory Quality Control Manager. The Laboratory Quality Control Manager summarizes the results in a report to the Corporate QA Manager who reports to upper management.

12.2 Periodic In-House Audits

In-house auditing is conducted by the Corporate QA Manager, and the National Laboratory QC Manager with the assistance of the Laboratory QC Coordinator. These audits occur at least every six months, and typically focus on a specific project. In-house audits take two forms - performance audits and systems audits. Performance audits involve submittal of blind spikes to the laboratory by the Quality Assurance Department for assessment of analytical accuracy. Systems audits consist of a thorough review of project procedures and documentation to confirm that work was performed in accordance with the Quality Assurance Project Plan and that adequate documentation exists to satisfy the project requirements.

12.2.1 Performance Audits

Audit Standards

As required on specific projects, the Quality Assurance Division provides spikes for analysis as independent check samples (audit standards). The QA Department prepares any audit standards that can be prepared readily from relatively non-hazardous, neat materials or certified concentrated standards. In some cases, preparation of reliable audit standards requires special facilities and equipment due to the hazardous nature of the materials and/or the requirement for precise measurement of minute quantities. In such cases, audit standards are obtained from the USEPA, Environmental Monitoring and Support Laboratory (EMSL), Cincinnati, Ohio, or from an equivalent source. The nature of the audit standards and the frequency of performance audits are specified in the Quality Assurance Plan of each project for which performance auditing is required. When practical, audit standards are provided in matrices resembling real project sample matrices, and undergo the full sample preparation and analysis procedure. However in many cases this is impractical, and it is necessary to submit audit samples as extracts, for analysis only. All measurable constituents in the audit standards should be within the expected range of concentrations to be encountered in the real samples (or in the extracts). They must be within the linear calibration range of the analytical equipment to be used.

Documentation

Performance audit standards are submitted to the Laboratory Quality Control Coordinator by the Quality Assurance Manager or the Project Quality Assurance Officer, in the appropriate, labeled containers. The label on each audit standard contains the following information (as applicable):

ERT-Prepared Standards

- Date prepared
- Initials of preparer
- Project number
- Audit standard number
- Analysis to be performed

EPA-Supplied Standards

- EPA EMSL identification number
- Project number
- Audit standard number
- Analytical method to be employed

All audit standards submitted to the Laboratory are logged in the Quality Assurance Department in a bound logbook. The following information is entered for each standard:

- Project number
- ERT audit standard number
- EPA EMSL identification number (if applicable)
- Date prepared or received
- Description of matrix
- Name and quantity of each measurable constituent
- Identification and expiration date of each primary standard used
- Identification of any analytical equipment used (e.g. analytical balance)
- Date submitted to laboratory
- Analytical method to be employed

Interpretation of Performance Audit Results

The audit standards are analyzed by the same procedures as the real samples. Analytical results are included in the analytical data packages.

The Project Quality Assurance Officer obtains the analytical results from the Laboratory Quality Control Coordinator and compares them to the true concentrations entered for each audit standard in the Quality Assurance Logbook. For each measurable constituent of each audit standard the percent recovery is determined. These results are interpreted as the accuracy of analyses represented by the performance audit.

12.2.2 Systems Audits

There are two different types of laboratory systems audits. Systems audits of laboratory operations (Operations Audits) are performed at a minimum frequency of once every six months. Operations audits address general laboratory operations and conformance to the applicable methodologies.

Systems Audit Procedures

The systems audits are performed by the Quality Assurance Manager or his qualified designee. The Laboratory Quality Control Coordinator participates in the audits as the laboratory's representative. It is the QC Coordinator's responsibility to provide the auditor with access to relevant data files, facilities and records, and to assist the auditor in obtaining an objective assessment.

Audit checklists are used to ensure that all salient points are addressed and documented. The checklists are filled out legibly and reproducibly, in ink, by the auditor, and are signed and dated by the auditor when completed. The operations audit checklist is based on EPA laboratory evaluation criteria.

Audit checklists will cover at least the following areas:

- Operations Audit

- Personnel qualifications and training records
- Adequacy of laboratory facilities, including work space, lighting, ventilation, and supplies
- Organization of lab facilities, including cleanliness, chemical storage, and waste disposal
- Maintenance and calibration recordkeeping for analytical equipment

- Safety (facility configuration and practices)
- General operations, including glassware cleaning, inventory and checking of reagents and standards, and storage procedures
- Recordkeeping, including sample log-in and tracking, traceability of standards, control charts, data packages, and organization of filing system
- Project Audit
 - Sample log-in and chain-of-custody records
 - Sample storage procedures and records
 - Sample preparation and analysis procedures
 - Method validation (where applicable)
 - Control charts
 - Precision and accuracy assessment
 - Method blanks, reagent blanks, duplicates, check samples, fortifications, surrogates, etc.
 - Calibration
 - Data packages
 - Analyst qualifications
 - Data validation and reporting

13. PREVENTIVE MAINTENANCE

Since instrumental methods of analysis require properly maintained and calibrated equipment, the operation and maintenance of modern analytical instrumentation is of primary importance in the production of acceptable data. In order to provide this data, ERT subscribes to the following programs:

- maintenance agreements/service contracts with instrument manufacturers
- laboratory preventive maintenance program

13.1 Service Contracts

Analytical equipment utilized by ERT laboratory personnel for this project are covered by maintenance agreements with the instrument manufacturers. These manufacturers provide for both periodic "preventive" service calls as well as the non-routine or emergency calls.

13.2 Instrument Logbooks

Individual instrument logbooks are maintained for each piece of equipment and located near the instrument. General information contained in the logbooks include:

- Inventory information:
equipment name, model number, serial number, manufacturer, date of acquisition, original cost
- Service tasks and intervals:
cleaning, calibration, operation based on the manufacturer's recommended schedule, and previous laboratory experience
- Service record:
date of breakdown, date of return to service, downtime, problems, repairs, cost of repairs, who performed the repairs, parts required, etc.
- calibration/performance checks
- daily operational notes

Analysts are referred to manufacturers' operating manuals for specific procedures to be followed in the operation and/or maintenance of the individual instruments.

Laboratory preventive maintenance includes any tasks that can be performed in-house, i.e., systematic cleaning of component parts as recommended in the instrument manual. If problems cannot be corrected by laboratory personnel, the instrument service representative is contacted and a service call requested to correct the problem.

14. SPECIFIC PROCEDURES TO ASSESS DATA PRECISION, ACCURACY AND COMPLETENESS

A quality control program is a systematic process that controls the validity of analytical results by measuring the accuracy and precision of each method and matrix, developing expected control limits, using these limits to detect errors or out-of-control events, and requiring corrective action techniques to prevent or minimize the recurrence of these events.

14.1 External and Internal Components

The accuracy and precision of sample measurements are influenced by both external and internal factors. External factors or errors are those associated with field collection and sample transportation. Internal factors or errors are those associated with sample preparation and analysis. External factors are defined briefly in Section 14.1.1. Internal factors are defined in Section 14.1.2. These internal components associated with laboratory practices, procedures, and controls of data quality confidence are presented in further depth.

14.1.1 External Components: Accuracy and Precision Measurements

The results for quality control samples taken in the field represent the best estimates of accuracy and precision for the samples, since these values reflect the entire process from sample collection through sample analysis. Below is a brief description of the information provided by each of these control samples:

- Field matrix spike - provides an estimate of bias based on recovery; includes matrix effects associated with sample preservation, shipping, preparation, and analysis.
- Field collected samples or replicates - independent samples collected at the same point in space and time. These give the best measurement of precision for sample collection through analysis.
- Field duplicate - a sample that has been divided into two or more portions. The analytical values obtained for each of these portions gives a second best measurement of precision for the entire sampling and analysis scheme.

14.1.2 Internal Components: Accuracy and Precision Measurements

The results of quality control samples created in the laboratory represent estimates of analysis and precision for the preparation and analysis steps of sample handling. This section describes the quality control-type information provided by each of these analytical measurements. The frequency of each of these measurements is discussed in Section 11.0, Internal Quality Control Checks.

Accuracy Measurements

- Laboratory fortifications - provide an estimate of bias based on recovery of the compounds analyzed for the sample batch, incorporating matrix effects associated with sample preparation and analysis.
- Surrogates - provide an estimate of bias based on recovery of similar compounds, but not the compounds analyzed, for each sample, incorporating matrix effects associated with sample preparation and analysis.
- Internal standard - an analyte that has the same characteristics as the surrogate, but is added to each sample in a batch, just prior to analysis. It measures bias or change in instrument performance from sample to sample, incorporating matrix effects associated with the analysis process only.
- Analysis matrix spikes - The analysis matrix spike is added prior to analysis. These spikes are similar to the internal standard; however, the analyte used is the same as that being analyzed and usually is added to a selected few samples in a batch of analyses. It incorporates matrix effects associated with the analysis step only.

Precision Measurements

- Laboratory duplicates - a sample that has been homogenized and split into two equal portions before the method sample preparation process. It measures sample precision associated with the preparation through analysis.
- Analysis replicate - a sample solution or extract that has been split before analysis; measures sample precision associated with the analysis only.

14.2 Control Charts

Control charts are quality control tools which graphically display the progression or movement of similar points taken at regular intervals in a process or over time. Both accuracy and precision control charts are maintained for each method and matrix.

14.2.1 Accuracy

Accuracy charts are maintained for surrogate and laboratory fortification recoveries. Each sample is identified by the date it was prepared and analyzed and its ERT sample number. The amount for each method and matrix is approximately five times the MDL. Values are plotted as percent recovered by computer program on an x-y graph. The mean, warning and control limits are presented graphically to enable a concise review of accuracy of the analysis.

14.2.2 Precision

Precision charts are maintained for laboratory duplicates. Both samples are identified by the date(s) prepared and analyzed and their ERT number. Values are plotted as percent difference on an x-y graph. The mean, warning and control limits are presented graphically to enable review of the precision of the analysis.

14.2.3 Limits

Both upper and lower warning limits and upper and lower control limits are established to aid in interpreting a suspicious or an out-of-control event. Warning limits express a narrower confidence interval and are used to warn the analyst or supervisor of possible system inconsistencies or failures, before an out-of-control event occurs. Control limits express the outer limits of expected method variability.

14.3 Suspicious/Out-of-Control Events

Graphing and connecting successive data points on control charts enables the laboratory to detect many types of suspicious and out-of-control situations. These events can be caught by monitoring for the following: outliers (suspicious and out-of-control), runs (suspicious), trends (suspicious), and periodicity (suspicious).

14.3.1 Outliers

There are two types of outliers: any particular point that falls outside the control limits or any point that falls outside the warning limits. A point that falls outside the control limits is classified as an out-of-control event; a point that falls outside the warning limits is classified as a suspicious event.

14.3.2 Runs

A run is defined as a series of points that line up on one side of the central line (the mean). Any run that has a length of seven points is indicative of a potential abnormality in the process, a suspicious event. A run can suggest several potential problems such as a leak in the system, elevated contamination, or incorrect dilutions of standards.

14.3.3 Trends

A trend is defined as a series of points that are marked by an unbroken rise or fall. Any trend with a length of five points is classified as a suspicious event. A trend may indicate a change in instrument sensitivity due to a dirty source or injection port or standard degradation, to name a few.

14.3.4 Periodicity

Periodicity is a term used to describe a recurring pattern of change over equal intervals. This occurrence may be of any length or amplitude; thus, careful observation of the control chart is necessary.

14.4 Completeness

The City will submit to EPA a minimum of 90% of the analytical data required under this QAPP, with the following exception. Analytical data required for active drinking water sources will be 100% complete.

15. CORRECTIVE ACTION

Corrective actions are required whenever an out-of-control event or potential out-of-control event is noted. The investigative action taken is somewhat dependent on the analysis and the event.

Generally, out-of-control events or potential out-of-control events are noted on an out-of-control event form (see Figure 15-1). This form is part of the data package and, thus, must be completed prior to data approval. If an out-of-control event does occur during analysis, for instance, a surrogate recovery falls outside the expected range, the analyst must describe on this form: the event, the investigative and corrective action taken, and the cause of the event, and notify the laboratory quality control coordinator (QCC). In some cases, investigation of an out-of-control event will reveal no problems. In such cases, only the event and the investigative action is recorded. If an out-of-control event is discovered during data package review, the QCC notifies the supervisor for corrective action.

15.1 Low-level PAH Analyses/Extended Analyses/Non-Criteria PAH Analyses

15.1.1 Surrogates

The laboratory will use the surrogates: naphthalene-d₈; fluorene-d₁₀ and chrysene-d₁₂ at a sample concentration level of 10 ng/L (ppt) or 20 ug/L (ppb). ERT will calculate the percent recovery of each surrogate for each sample. Corrective action will be taken whenever the surrogate recovery for any one or more surrogates is outside the following acceptance criteria:

<u>Surrogate</u>	<u>Acceptance Criteria %</u>	
	<u>Low-level</u>	<u>Non-criteria</u>
Naphthalene-d ₈	14-108	25-175
Fluorene-d ₁₀	41-162	25-175
Chrysene-d ₁₂	10-118	25-175

The following corrective action will be taken when required as stated above:

- Check calculations to assure there are no errors;
- Check internal standard and surrogate solutions for degradation, contamination, etc., and check instrument performance;
- Reanalyze the sample or extract if the steps in part a) or b) fail to reveal a problem. If reanalysis of the extracts yields surrogate spike recoveries within the stated limits, then the reanalysis data will be used. Both the original and reanalysis data will be reported.

Figure 15-1 Out-of-Control Event Form

Date _____ Time _____ Analyst _____

Method _____ Matrix _____

Initials of individual initially notified _____

Suspect lab numbers _____

Out-of-control lab numbers _____

Indication of out-of-control event _____

Cause determined _____

Action taken _____

Date and time QAC notified _____

Date and time control resumed _____

Precision criteria met _____ Accuracy criteria met _____

Reanalysis of data completed _____

- d) If a), b) or c) do not correct the problem, the data for that sample will be reported but will not count towards satisfying the monitoring requirements of the RAP.

15.1.2 Matrix Spikes

ERT will use eight representative compounds spiked into a sample of water collected in the field. These compounds and the spiking levels are listed below:

	<u>PPT</u>	<u>PPB</u>
Naphthalene	100 ng/L	50µg/L
Fluorene	20	50
Chrysene	20	50
Benzo(g,h,i)perylene	20	50
Indene	20	50
Quinoline	20	50
Benzo(e)pyrene	20	50
2-methyl naphthalene	20	50

Naphthalene is spiked at a higher level in the ppt method, because of the higher method detection limit.

The matrix spike criteria for data validity are as follows:

- The average of the percent recoveries for all eight compounds must fall between 20 and 150 percent.
- Only one compound can be below its required minimum percent recovery. These minimum percent recoveries are:
 - 1) 10% for chrysene, benzo(g,h,i)perylene, and benzo(e)pyrene, and
 - 2) 20% for all other compounds.

If the matrix spike criteria are not met, the matrix spike analysis will be repeated. If the subsequent matrix spike analysis meets the criteria, the data will be considered valid. Both matrix spike and surrogate spike recoveries will be used in assessing quality assurance/quality control for ERT's analytical work.

15.2 Extended Analyses for Phenolics in GAC Plant

15.2.1 Surrogates

The laboratory will spike all samples with a minimum of three surrogate compounds and calculate the percent recoveries. On-going quality control charts plotting surrogate percent recoveries will be prepared. The control charts will be updated as sample surrogate recoveries are plotted, as a

means of observing trends or changes in method precision. Control charts will be used to alert ERT to the need to check method procedures, but the failure of a surrogate to fall within the 95% confidence limits of the ongoing control charts does not necessarily invalidate the sample data.

15.2.2 Matrix Spikes

The percent recovery for each parameter in the matrix spike will be compared with the corresponding QC acceptance criteria shown in Table 15-1. If any individual recovery falls outside the designated ranges, that parameter has failed the criteria. If any parameter fails the acceptance criteria for recovery, a QC check standard containing each parameter that failed must be prepared and analyzed. The QC check sample will be prepared at a concentration of 100 ug/L for each parameter which failed, in deionized water. The QC check sample will be analyzed and the percent recovery for each parameter calculated.

The percent recovery for each parameter in the QC check sample will be compared to the acceptance criteria in Table 15-1. If the recovery of any parameter falls outside the designated range, the analytical result for that parameter in the original unspiked samples will be reported but will not count towards satisfying the monitoring requirements of the RAP.

15.3 Expanded Analyses

Table 15-2 shows the analytes to be measured for expanded analyses. This section discusses the criteria to be used for evaluating the results of the quality control analyses discussed in Section 11.3 and the corrective actions to be taken whenever a sample or samples fail to meet the criteria.

15.3.1 Volatile Organics

Volatile organics will be analyzed according to EPA Method 624 (see Appendix B), which contains specific quality control procedures and criteria. Corrective action will be taken whenever the results of the required quality control, as set forth in Section 8 of EPA 624, fail to meet the compound specific acceptance criteria given on Table 5 of EPA 624.

The percent recovery for each parameter in the matrix spike will be compared with the corresponding QC acceptance criteria shown in Table 5 of EPA 624. If any individual recovery falls outside the designated ranges, that parameter has failed the criteria.

If any parameter fails the acceptance criteria for recovery, a QC check standard containing each parameter that failed must be prepared and analyzed. The QC check sample will be prepared at a concentration of 100 ug/L for each parameter which failed in deionized water. The QC check sample will be analyzed and the percent recovery for each parameter calculated.

TABLE 15-1
ACCEPTANCE CRITERIA - EXTENDED ANALYSES FOR PHENOLICS¹

<u>Parameter</u>	<u>Acceptance Criteria</u> <u>(%)</u>
4-chloro-3-methylphenol	22-147
2-chlorophenol	23-134
2,4-dichlorophenol	39-135
2,4-dimethylphenol	32-119
2,4-dinitrophenol	D-191
2-methyl-4,6-dinitrophenol	D-181
2-nitrophenol	29-182
4-nitrophenol	D-132
Pentachlorophenol	14-176
Phenol	5-112
2,4,6-trichlorophenol	37-144

D = Detected; result must be greater than zero.

¹Reprinted from Table 6, page 43392 of "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act", Federal Register, Friday, October 26, 1984.

TABLE 15-2
EXPANDED ANALYSES ANALYTE LIST AND
METHOD REFERENCE

<u>Analytes</u>	<u>Method Reference</u>
Volatile Organics	EPA 624 ¹
Acid, Base/Neutral Extractable Organics	EPA 625 ¹
Priority Pollutant Metals	EPA 200.7, 204.2, 206.2, 245.1, 270.2, 279.2 ²
Ammonia	EPA 350.2 ²
Chloride	EPA 325.2 ²
Sodium	EPA 200.7 ²
Sulfate	EPA 375.4 ²
Total Phenol	335.2 ²
Cyanide	335.2 ²

¹ "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act" Federal Register, Friday, October 26, 1984.

² "Methods for Chemical Analysis of Water and Wastes" EPA-600/4-79-020, March 1979 (Revised March 1983).

The percent recovery for each parameter in the QC check sample will be compared to the acceptance criteria in Table 5 of EPA 624. If the recovery of any parameter falls outside the designated range, the analytical result for that parameter in the original unspiked samples will be reported but will not count towards satisfying the monitoring requirements of the RAP.

The laboratory will also spike all samples with a minimum of three surrogate compounds and calculate the percent recoveries. On-going quality control charts plotting surrogate percent recoveries will be prepared. The control charts will be updated as sample surrogate recoveries are plotted, as a means of observing trends or changes in method precision. Control charts will be used to alert ERT to the need to check method procedures, but failure of a surrogate to fall within the 95% confidence limits of the ongoing control charts does not necessarily invalidate the sample data.

15.3.2 Acid, Base/Neutral Extractable Organics

Extractable organics will be analyzed according to EPA Method 625 (see Appendix B). EPA Method 625 contains detailed quality control procedures. All samples analyzed for extractable organics will include the quality control requirements outlined in Section 8 of EPA 625. Corrective action will be taken whenever the matrix spike recovery compounds (a rotating representative group of 10-12 parameters) fall outside the ranges for acceptance criteria in Table 6 of EPA 625. If any parameter fails the acceptance criteria for recovery, a QC check standard containing each parameter that failed must be prepared and analyzed. The QC check sample will be prepared at a concentration of 100 ug/L for each parameter which failed, in deionized water. The QC check sample will be analyzed and the percent recovery for each parameter calculated.

The percent recovery for each parameter in the QC check sample will be compared to the acceptance criteria in Table 6 of EPA 625. If the recovery of any parameter falls outside the designated range, the analytical result for that parameter in the original unspiked samples will be reported but will not count towards satisfying the monitoring requirements of the RAP.

The laboratory will also spike all samples with a minimum of three surrogate compounds and calculate the percent recoveries. On-going quality control charts plotting surrogate percent recoveries will be prepared. The control charts will be updated as sample surrogate recoveries are plotted, as a means of observing trends or changes in method precision. Control charts will be used to alert ERT to the need to check method procedures, but failure of a surrogate to fall within the 95% confidence limits of the ongoing control charts does not necessarily invalidate the sample data.

15.3.3 Priority Pollutant Metals

Priority pollutant metals method references are shown on Table 15-2. All samples analyzed for metals will follow the detailed quality control procedures outlined in the individual methods. The methods are included in Appendix B. Corrective action will be taken whenever the percent recovery for individual metals for matrix spikes is outside the range of 75-125%. Whenever a matrix spike fails to meet the criteria for any metal, the following corrective action will be taken:

- a) Check calculations to assure there are no errors.
- b) Check standards for degradation, contamination, etc., and check instrument performance.
- c) If the steps in (a) or (b) fail to reveal a problem, a QC check sample will be prepared by spiking deionized water with those metals which failed to meet the criteria in the original matrix spike.
- d) The QC check sample will be analyzed and the results compared to the criteria. If the QC check standard meets the criteria no further corrective action will be taken.
- e) If any metal contained in the QC check standard fails the criteria, the data for that metal for those samples associated with the matrix spike will not be valid.

15.3.4 Other Inorganics

Method references for ammonia, chloride, sodium, sulfate, total cyanide, and total phenol are shown on Table 15-2. All samples analyzed for these parameters will follow the quality control procedures outlined in those methods and discussed in Section 11.3 of the QAPP. The methods are included in Appendix B. Corrective action will be taken whenever the percent recovery for the analyte in question for matrix spikes is outside the range of 75-125%. Whenever a matrix spike fails to meet the criteria the following corrective action will be taken:

- a) Check calculations to assume there are no errors.
- b) Check standards for degradation, contamination, etc., and check instrument performance.
- c) If the steps in (a) or (b) fail to reveal a problem, a QC check standard will be prepared by spiking deionized water with the analyte in question.
- d) The QC check standard will be analyzed and the result compared to the criteria. If the QC check standard meets the criteria no further corrective action will be taken.
- e) If the QC check standard fails the criteria, the data for samples associated with that matrix spike for the analyte in question will be considered invalid.

15.4 Other Corrective Actions

These sections discuss corrective actions which will be taken in the event that a sample or sample extract is lost or destroyed during shipment, storage or analysis, or in performance and system audits.

15.4.1 Samples

In order to minimize the possibility of sample destruction during shipment, six 1-liter bottles will be taken for all low-level (ppt) samples. For all samples, field blanks, duplicates, and matrix spikes, subsequent extraction and analysis will be conducted on four intact 1-liter bottles. All field blanks will be collected in duplicate. One field blank will be analyzed with the sample set and the duplicate will be extracted and held. In the event that the field blank is lost during analysis or invalidated, the duplicate field blank will be analyzed and reported.

If less than four liters of a sample remains after shipment and storage for analysis, the City will be notified and another sample will be collected and shipped to the laboratory for analysis. The analysis report for the sample batch containing the affected sample will clearly note in the discussion section that a replacement sample was taken.

15.4.2 Sample Extracts

If a sample extract is broken or lost during analysis, the City will be notified and another sample will be collected and shipped to the laboratory for analysis if necessary, depending upon the data completeness requirements for the specific sample type. The analysis report for the sample batch containing the affected sample will clearly note in the discussion section that a replacement sample was taken.

15.4.3 Quality Control Samples

If a solvent blank, method blank, or matrix spike is lost or broken during analysis, a replacement QC sample will be sampled and analyzed. The analysis report will clearly note that a replacement QC sample was analyzed.

If a field blank is lost or broken during shipment, storage, or analysis, no replacement will be analyzed. The analysis report for the sample batch associated with the field or shipping blank will clearly note in the discussion section why the data is unavailable. If the interpretation of the data from samples associated with the affected field blank warrant it, resampling of the entire batch may be conducted. This decision would be reached by concurrence of the EPA, MPCA and City project leaders.

15.4.4 Performance and System Audits

Each systems audit is immediately followed by a debriefing, in which the auditor discusses his findings with the laboratory representatives. The debriefing serves a two-fold purpose. First, laboratory management is afforded an early summary of findings, which allows them to begin formulating corrective strategies, and second, the auditor has a chance to test preliminary conclusions and to correct any misconceptions before drafting his report.

The systems audit report (which may or may not contain performance audit findings) is first issued in draft to the Laboratory Quality Control Coordinator. The QC Coordinator distributes the draft to the Laboratory Manager and appropriate supervisors to solicit comments and/or rebuttals. These responses are forwarded, in writing, to the auditor. The auditor makes revisions to the draft, on the basis of these responses, at his discretion. Any points of disagreement between the QA department and the laboratory organization are resolved through discussion before the final report is issued. Written responses to the draft report are attached to the final report as an appendix.

Final audit reports are issued to project management and to corporate management. Items requiring corrective action are documented on a Corrective Action Request Form addressed to the project manager. One copy is retained by QA upon issuance. The project manager receives the original and one copy. When satisfactory progress has been achieved on each requested action, the project manager or designee enters descriptions of actions and results on the form, then retains the copy and returns the original to QA to close the loop.

Results of interlaboratory performance surveys and in-house audits, along with unresolved corrective action items are summarized in a quarterly report from the Quality Assurance Manager to the Executive Vice President.

16. QUALITY ASSUARANCE REPORTS TO MANAGEMENT

The ERT Quality Assurance Department is completely independent of line function. Its manager reports directly and exclusively to the ERT Executive Vice President. The Laboratory Quality Control Coordinator is appointed by the Chemistry Division Quality Control Manager who reports directly to the Division Director with ancillary responsibilities to the Laboratory Manager and the Corporate Quality Assurance Manager.

Reports summarizing any changes in quality control procedures and guidelines, updated control limits and any deviations are made on a periodic basis to both laboratory and corporate management. These occur through a regular quarterly report from the Laboratory QC Coordinator to the Division QC Manager. Copies of this report are also submitted to the Corporate QA Manager, the Division Director, the Laboratory Manager and Supervisors. Should the circumstances warrant more frequent communication between the laboratory QCC, the QC Manager or any other persons in management, both verbal and written communication will be implemented.

16.1 Performance and System Audits

Final performance and system audit reports are issued to project management and to corporate management. Items requiring corrective action are documented on a Corrective Action Request Form addressed to the project manager. The Corrective Action Request is a three-part NCR-type form. The first copy is retained by the Quality Assurance Department upon issuance. The project manager receives the original and one copy. When satisfactory progress has been achieved on each requested action, the project manager or designee enters descriptions of actions and results on the form, then retains the copy and returns the original to the Quality Assurance Department to close the loop.

Results of interlaboratory performance surveys and in-house audits, along with unresolved corrective action items are summarized in a quarterly report from the Quality Assurance Manager to the Executive Vice President.

10.3.2 Sampling Report

The sampling report will contain the following information associated with each sample and sample analysis:

- 1) Field Identification Designation
- 2) ERT Laboratory Sample Number
- 3) Field Logbook/Page Number
- 4) Date of Collection
- 5) Date Received at ERT
- 6) Date Extracted
- 7) Date Analyzed
- 8) GC/MS File #
- 9) GC/MS Tape #
- 10) Corresponding DFTPP File #
- 11) Corresponding Matrix Spike Sample #
- 12) Corresponding Method Blank Sample #
- 13) Corresponding Solvent Blank Sample #
- 14) Corresponding GC/MS Calibration Standard File #
- 15) Description of any problems encountered

10.3.3 Analytical Results Report

Each analytical results report will contain the following:

- 1) Field Identification Designation
- 2) ERT Laboratory Sample Number
- 3) Analytical Results (ppt or ppb), in terms of a) individual PAH identification and quantitation b) Total Carcinogenic PAH c) Total Other PAH and d) Total PAH

The analytical results report will be validated and signed by the Laboratory Manager.

List of Carcinogenic PAH and Other PAH

The analytical method will provide for identification and quantitation of two groups of target compounds - the Carcinogenic PAH and the other PAH group. Listed in Table 10-1 are the two groups of target compounds. Analytical results will be reported for individual compounds, with the exception of the three benzofluoranthene isomers (b,j, and k). Due to the difficulty in maintaining chromatographic separation of this isomeric series, a total benzofluoranthenes analytical result will be reported (unless advances in chromatographic technology allow for separation in the future). This benzofluoranthenes quantitative result will be utilized in the calculation of total carcinogenic PAH.

TABLE 10-1
STANDARD PAH AND OTHER PAH COMPOUNDS
FOR IDENTIFICATION AND QUANTITATION

a. Carcinogenic PAH

<u>Compound</u>	<u>Chemical Abstract Service Registry No.</u>
benzo(a)anthracene	(56-55-3)
benzo(b)fluoranthene	(205-99-2)
benzo(j)fluoranthene	(205-82-3)
benzo(k)fluoranthene	(207-08-9)
benzo(ghi)perylene	(191-24-2)
benzo(a)pyrene	(50-32-8)
chrysene	(218-01-9)
dibenz(a,h)anthracene	(53-70-3)
indeno(1,2,3-cd)pyrene	(193-39-5)
quinoline	(91-22-5)

b. Other PAH

<u>Compound</u>	<u>Chemical Abstract Service Registry No.</u>
acenaphthene	(83-32-9)
acenaphthylene	(208-96-8)
acridine	(260-94-6)
anthracene	(120-12-7)
2,3-benzofuran	(271-98-6)
benzo(e)pyrene	(192-97-2)
benzo(b)thiophene	(95-15-8)
biphenyl	(92-15-8)
carbazole	(86-74-8)
dibenzofuran	(132-64-9)
dibenzothiophene	(132-65-0)
2,3-dihydroindene	(496-11-7)
fluoranthene	(206-44-0)
fluorene	(86-73-7)
indene	(95-13-6)
indole	(120-72-9)
1-methylnaphthalene	(90-12-0)
2-methylnaphthalene	(91-57-6)
naphthalene	(1-20-3)
perylene	(198-55-0)
phenanthrene	(85-01-08)
pyrene	(129-00-0)

Analytical Results Reporting Protocol

The quantitative results for any of the identified target compounds will be reported in one of three possible ways. Concentrations of analytes equal to or greater than the method detection limit (MDL) will be assigned a numerical concentration value reported to two (2) significant figures (i.e. 52 ng/L). Concentrations of analytes identified as present at a level less than the MDL but equal to or greater than the lower confidence limit (LCL) of the 95% confidence interval of the MDL are reported as less than the MDL (<MDL, i.e. <3.0 ng/L). Concentrations of target analytes less than the LCL (95% confidence interval) of the MDL are reported as not detectable (i.e. ND). In all cases, the quantitative results will be corrected for levels observed in the method blank, as described in Section 11.2. An example of this report is included as Figure 10-2.

10.3.4 Surrogate Recovery Report

Each surrogate recovery report will contain the following:

- 1) Field Identification Designation
- 2) ERT Laboratory Sample Number
- 3) Spiking concentration for each of the three deuterium labelled surrogate compounds (naphthalene-d₈, fluorene-d₁₀, chrysene-d₁₂)
- 4) Percent recovery result for each of the three surrogate compounds.

An example of this report is included as Figure 10-3.

10.3.5 Matrix Spike Recovery Report

Each matrix spike recovery report will contain the following:

- 1) Field identification designation
- 2) ERT laboratory sample number
- 3) Spiking concentrations for each of the eight compounds selected (naphthalene, fluorene, chrysene, benzo(g,h,i) perylene, indene, quinoline, benz(e)pyrene, and 2-methylnaphthalene).
- 4) Percent recovery results for all the method spike compounds.
- 5) Average percent recovery for the group of eight compounds spiked.

An example of this report is included as Figure 10-4.

10.3.6 Reporting Requirements for Samples Exceeding Advisory Levels or Drinking Water Criterion

For active drinking water wells, ERT will notify the City of St. Louis Park by telephone, within 24 hours of completing an analysis, whenever a sample analysis is shown to exceed the following Advisory Levels or Drinking Water Criterion:

ERT STANDARD OPERATING PROCEDURE

Number: 7320

Date of Issue: March 12, 1984

Title: Calibration and Operation of Hydrolab Water
Quality Monitor

Organizational Acceptance

Authorization

Date

Originator

Department Manager

Divisional Manager

Group Quality Assurance Officer

Other

Alberta Lyons

3/13/84

Revisions

Changes

Authorization

Date

STANDARD OPERATING PROCEDURE

Page 1 of 8

Title: Calibration and Operation of Hydrolab Water Quality Monitor

Date: 1st Qtr 198
Number: SOP 7320
Revision: 1

1.0 Applicability

This Standard Operating Procedure (SOP) provides basic instructions to be employed for the field operation of Hydrolab digital multimeters (Model Nos. 4041 and 8000). Hydrolabs are used for field measurement of water-quality parameters.

2.0 Responsibilities

The field team is responsible for ensuring that the Hydrolab unit is in proper operating condition prior to use in the field. All system-calibration checks are the responsibility of the field team.

3.0 Materials

- Hydrolab Operation and Maintenance Instruction Manual
- Hydrolab Sonde unit, battery pack and surface unit
- Hydrolab calibration-cup
- Two Fisher-brand laboratory potassium chloride (KCl) standard solutions (known conductivity at 25°C)
- Two freshly prepared pH buffer solutions. Generally pH 7.0 and pH 4.0 or 10.0 are used.
- Distilled or de-ionized water (approximately two liters)
- Chemical-free paper towels
- Screwdrivers (as supplied in the Hydrolab Accessory Kit)

4.0 Procedures

The Hydrolab provides simultaneous measurement of four water quality parameters; 1) dissolved oxygen, in mg/l, 2) temperature, in °C; 3) pH, in standard units, and 4) conductivity, in umhos/cm (uS/cm). The panel switch on the front of the indicator unit controls which parameter is being measured and read-out.

The display is read in the following manner; temperature, pH and dissolved oxygen are read out directly. For example, a temperature of 21.8°C will be displayed as 21.8. A dissolved oxygen (D.O.) or pH reading of 8.1 will be displayed as 08.1. Conductivity is read out directly on the 2k scale. If the 20k scale is required to measure higher conductivity the number that is displayed will need to be

0888J

STANDARD OPERATING PROCEDURE

Page 2 of 8

Title:

Calibration and Operation of Hydrolab Water Quality Monitor

Date: 1st Qtr 198
Number: SOP 7320
Revision: 1

multiplied by 10. In the 200k scale the reading will be multiplied by 100. For example, suppose the sample being measured has a conductivity of 1527 uS/cm. Using the 2k scale, the display will show 1527 (direct read-out). Using the 20k scale the display will show 153 ($153 \times 10 = 1530$ uS/cm). Using the 200k range the display will show 015 ($015 \times 100 = 1500$ uS/cm). Only the Hydrolab model 4041 offers the three scale measurement. The Hydrolab model 8000 is restricted to measurement of conductivity within the range of 0-2000.

4.1 Hydrolab Calibration

A complete calibration check should be performed before going to and after returning from a field sampling/water quality measurement activity. The calibration procedures should be carried out in a controlled environment such as a laboratory, but a field office or closed-in shelter may also be used.

At least one hour prior to calibration, take the following preparatory steps:

- 1) Remove the "Storage-Cup" from the Sonde Unit.
- 2) Remove the protective guard from the dissolved oxygen sensor.
- 3) Install the "Calibration-Cup" on the Sonde Unit and fill to the brim with distilled water.
- 4) Seal the Calibration Cup with the soft plastic cap and store the sonde unit, calibration standards, and the distilled water at constant room temperature for at least one hour in order to bring the various sensors, temperature compensating elements, and the calibration solutions into thermal equilibrium (within a few degrees).

All of the calibration controls are located on the front panel of the Indicator Unit. Adjustments, if necessary, should be made in the following manner:

- 1) Remove the appropriate seal-screw for the parameter being adjusted.
- 2) Insert a small screwdriver through the access hole and adjust the calibration control in the direction which brings the reading into agreement with the value of the standard solution being employed.
- 3) Replace the seal-screw.

0888J

STANDARD OPERATING PROCEDURE

Page 3 of 8

Title:

Calibration and Operation of Hydrolab Water Quality Monitor

Date: 1st Qtr 1984
Number: SOP 7320
Revision: 1

A RINSE STEP will be used several times during the calibration procedure. It is to be performed in the following manner: Fill the calibration cup halfway with de-ionized or distilled water. Snap on the soft plastic cap; shake the sonde unit for ten seconds and then pour out the water. Repeat twice more using fresh de-ionized or distilled water. Remove the cup and shake as much of the rinse water as possible from the electrodes.

4.1.1 Dissolved Oxygen Calibration

The Dissolved Oxygen system is the first to be calibrated since the water that has been stored in the calibration cup is used to maintain control of the temperature inside the cup. The calibration standard is either a water sample of a known D.O. concentration (determined in the laboratory by the Winkler or iodometric method in accordance with Standard Methods for the Examination of Water and Wastewater, 15th Edition, APHA-AWWA-WPCF, 1980 or water-saturated air at the temperature inside the calibration cup. The following procedures are for the water-saturated air method for D.O. calibration.

Invert the Sonde Unit and remove the soft plastic cap. Pour off enough water to bring the level to just below the D.O. membrane- retainer O-ring. With a clean paper towel or tissue blot any moisture from the D.O membrane. Cover the calibration cup mouth with one of the hard plastic caps provided in the Accessory Kit. This will keep drafts from blowing on the membrane. Do not seal the cup with the plastic cap, because that could cause a partial-pressure change in the cup. Wait approximately 5 minutes, or until the reading is stable, then switch to the TEMPERATURE position and record the temperature reading. Refer to Table 1 for the correct oxygen concentration at this temperature. Since the table values refer to concentrations at Standard Pressure it will be necessary to correct the value for local barometric pressure. This should be done in the following manner:

Correct D.O. Setting = (Local Barometric
Pressure/760mm) x (Table value
at Cup Temperature)

EXAMPLE: If T = 28.5°C and Local Barometric
Pressure = 800mm,

Correct D.O. Setting = (800mm/760mm) x (7.6 mg/l)
= 8.0 mg/l

0888J

STANDARD OPERATING PROCEDURE

Page 4 of 8

Title:

Calibration and Operation of Hydrolab Water Quality Monitor

Date: 1st Qtr 198
Number: SOP 7320
Revision: 1

If a barometer is not available, the equivalent pressure may be estimated from Table 2 which relates atmospheric pressure with elevation above mean sea level. Therefore, the approximate atmospheric pressure at an altitude of 2000 feet, for example, would be: Local Atmospheric Pressure = 705mm Hg.

Adjust the Dissolved Oxygen calibration control until the proper value (rounded to nearest tenth) is displayed. Pour out the water; and then follow with a RINSE STEP.

4.1.2 pH Calibration

Calibrating the pH system requires the use of two Fisher-brand pH laboratory buffer solutions. Depending upon the application, either pH 4.0 or pH 10.0 is used in addition to pH 7.0. Invert the sonde unit and fill the calibration cup with fresh pH 7.0 buffer solution. Switch to "pH", and wait approximately 5 minutes for thermal equilibrium. Then adjust the pH calibration control until 7.0 is displayed on the read-out.

Pour out the 7.0 buffer and repeat the RINSE STEP. Invert the sonde unit and screw on the calibration cup; fill with 10.0 or 4.0 buffer. After approximately 5 minutes, adjust the pH "Slope" control until either 10.0 or 4.0 (as appropriate for the buffer being used) is displayed on the read-out. Pour out the buffer and repeat the RINSE STEP Two Times

4.1.3 Conductivity Calibration

After the second RINSE STEP, take a clean paper towel or tissue, and blot most of the moisture in the electrode area so that the standard will not suffer dilution.

Install a clean calibration cup and invert the sonde unit. The conductivity system is calibrated using at least two prepared KCl standard solutions with a known conductivity at 25°C. From Table 3, select two standard solutions with values of approximately one-third and two-thirds of the range you are most likely to encounter in the field. For example, if you are going to be working in fresh water (0-2K scale) you would want to use a 0.01M standard and a 0.005M standard. Select the more concentrated of the two standards and pour it slowly down the side of the calibration cup until full. When the reading is stable, adjust the conductivity calibration control until the display matches

0888J

STANDARD OPERATING PROCEDURE

Page 5 of 8

Title:

Calibration and Operation of Hydrolab Water Quality Monitor

Date: 1st Qtr 198
Number: SOP 7320
Revision: 1

the value listed in Table 3. Empty the calibration cup and repeat the RINSE STEP Two Times. Pour in the second standard. Check the reading on the Display. It should be correct within $\pm 1\%$ of the range being used. For example, if the 0-2K scale is used, the reading for the second standard should be correct within ± 20 uS/cm of the true value. Pour out the standard solution. Perform a RINSE STEP.

4.1.4 Temperature Calibration

The temperature system is factory calibrated and is accurate to $\pm 0.2^{\circ}\text{C}$. No calibration adjustment is provided. A periodic check of the temperature system against an NBS-traceable thermometer should be performed as a verification.

4.2 Final Preparation

Turn the system off and disconnect the system components. Replace all rubber dust caps. Remove the Calibration Cup from the Sonde Unit and replace the protective guard on the dissolved oxygen electrode. Fill the Storage Cup with tap water and install onto the Sonde Unit. The system is now calibrated and ready for field use.

4.3 Field Operation

Remove the Storage Cup from the calibrated sonde unit and install the guard or the optional sample circulator. Connect the system components. Lower the sonde unit into the water (sideways, if possible) and shake it to dislodge air bubbles trapped in the conductivity cell block. Release the sonde unit and lower it to sample depth. Wait until the readings stabilize (D.O. is the best indicator) and then record the value for each parameter. Repeat at new depths or locations.

When using for ground water sampling, pour/place a sample of ground water into the Storage Cup and attach it to the sonde so that all nodes are submerged.

Check the battery voltage occasionally; charge or change batteries if the level drops below 10.5 volts. DO NOT charge the battery routinely after each day's use. Doing so may shorten the life of the battery. Use the battery until the voltage level drops to between 10.5 and 11.0 volts. At this point put the battery on charge for 24 hours.

0888J

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1284b (12/78)

TABLE 1
DISSOLVED OXYGEN SATURATION VALUES IN
DISTILLED WATER AT 760 mm Hg

<u>Temp. (°C)</u>	<u>DO (mg/l)</u>	<u>Temp (°C)</u>	<u>DO (mg/l)</u>
0.0	14.6	15.5	9.9
0.5	14.4	16.0	9.8
1.0	14.2	16.5	9.7
1.5	14.0	17.0	9.6
2.0	13.9	17.5	9.5
2.5	13.7	18.0	9.4
3.0	13.5	18.5	9.3
3.5	13.3	19.0	9.2
4.0	13.1	19.5	9.1
4.5	13.0	20.0	9.0
5.0	12.8	20.5	8.9
5.5	12.6	21.0	8.8
6.0	12.5	21.5	8.8
6.5	12.3	22.0	8.7
7.0	12.1	22.5	8.6
7.5	12.0	23.0	8.5
8.0	11.8	23.5	8.4
8.5	11.7	24.0	8.3
9.0	11.6	24.5	8.2
9.5	11.4	25.0	8.2
10.0	11.3	25.5	8.1
10.5	11.1	26.0	8.0
11.0	11.0	26.5	8.0
11.5	10.9	27.0	7.9
12.0	10.8	27.5	7.8
12.5	10.6	28.8	7.7
13.0	10.5	28.5	7.6
13.5	10.4	29.0	7.6
14.0	10.3	29.5	7.5
14.5	10.2	30.0	7.4
15.0	10.0	30.5	7.4

TABLE 2

Site Elevation (Feet above mean sea level)	Approximate Mean Barometric Pressure (mm Hg)
1000	733
1500	720
2000	705
2500	694
3000	680
3500	669
4000	656
4500	644
5000	632
5500	620
6000	609
6500	598
7000	586
7500	575
8000	564
8500	554
9000	543
9500	533
10000	523

TABLE 3
CONDUCTIVITY CALIBRATION STANDARDS

Conductivities of Potassium Chloride Solutions at 25°C M.W. = 74.555			Conductivity Reading on Hydrolab Display for Given Range Setting (uS/cm)		
<u>Conc.</u>	<u>Grams KCl/L</u>	<u>uS/cm</u>	<u>(0-2K)</u>	<u>(0-20K)</u>	<u>(0-200K)</u>
0.0005	0.03728	73.9		-	-
0.001	0.07456	147.0	147	-	-
0.002	0.1491	292.0	292	-	-
0.005	0.3728	717.8	718	-	-
0.01	0.7456	1.413K	1413	141	-
0.02	1.491	2.767K	---	277	-
0.05	3.728	6.668K	---	667	-
0.1	7.456	12.90K	---	1290	129
0.2	14.911	24.82K	---	---	248
0.5	37.278	58.64K	---	---	586
1.0	74.555	111.9K	---	---	1119

NOTES:

(1) Two conductivity standards are recommended for each range setting (boxed-in values). Calibration adjustments will be made first with the higher concentration and then with the lower concentration.

(2) Single dashes indicate ranges which are not recommended for calibration checks.

(3) The Hydrolab model 8000 is restricted to conductivity readings between 0-2000 μ S/cm (0-2k scale), therefore conductivity readings and thus calibration solutions within the 0-20k and 0-200k ranges will not apply.



ERT STANDARD OPERATING PROCEDURE

Number: 7510

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Title: Packaging and Shipment of Samples

Organizational Acceptance

Originator

Department Manager

Divisional Manager

Group Quality Assurance Officer

Other

Authorization

Date

Stephen C. Calkins

3/13/84

Robert F. Fagan

3/13/84

Revisions

Changes

Authorization

Date

1.0 Applicability

This Standard Operating Procedure (SOP) is concerned with the presentation of protocols associated with the packaging and shipment of samples. Two general categories of samples exist: environmental samples consisting of air, water and soil; and waste samples which include non-hazardous solid wastes and hazardous wastes as defined by 40 CFR Part 261.

2.0 Responsibilities

It is the responsibility of the project manager to assure that the proper packaging and shipping techniques are entered into each project specific sampling plan. The site operations manager shall be responsible for the enactment and completion of the packaging and shipping requirements outlined in project specific sampling plans. The site operations manager shall be responsible to research, identify and follow all applicable U.S. Department of Transportation (DOT) regulations.

3.0 General Method

The objective of sample packaging and shipping protocol is to identify standard procedures which will minimize the potential for sample spillage or leakage and maintain field sampling program compliance with U.S. EPA and U.S. DOT regulations.

The extent and nature of sample containerization will be governed by the type of sample, and the most reasonable projection of the sample's hazardous nature and constituents. The EPA regulations (40 CFR Section 261.4(d)) specify that samples of solid waste, water, soil or air, collected for the sole purpose of testing, are exempt from regulation under the Resource Conservation and Recovery Act (RCRA) when all of the following conditions are applicable:

- A. Samples are being transported to a laboratory for analysis;
- B. Samples are being transported to the collector from the laboratory after analysis;
- C. Samples are being stored (1) by the collector prior to shipment for analyses, (2) by the analytical laboratory prior to analyses, (3) by the analytical laboratory after testing but prior to return of sample to the collector or pending the conclusion of a court case.

Qualification for categories A and B above require that sample collectors comply with U.S. DOT and U.S. Postal Service (USPS) regulations or comply with the following items if U.S. DOT and USPS regulations are found not to apply:

0908J

STANDARD OPERATING PROCEDURE

Title: Packaging and Shipment of Samples

Date 1st Qtr. 1984
Number SOP 7510
Revision

The following information must accompany all samples and will be entered on a sample specific basis on chain of custody records:

- sample collector's name, mailing address and telephone number,
- analytical laboratory's name, mailing address and telephone number,
- quantity of sample,
- date of shipment
- description of sample

In addition, all samples must be packaged so that they do not leak, spill or vaporize.

4.0 Method

- 4.1 Place plastic bubble wrap matting over the base and bottom corners of each cooler or shipping container as needed to manifest each sample.
- 4.2 Obtain a chain of custody record as shown in Figure 1 and enter all the appropriate information as discussed in Section 3.0 of this SOP. Chain of custody records will include complete information for each sample. One or more chain of custody records shall be completed for each cooler or shipping container as needed to manifest each sample.
- 4.3 Wrap each sample bottle individually and place standing upright on the base of the appropriate cooler, taking care to leave room for some packing material and ice or equivalent. Rubber bands should be used to secure wrapping, completely around each sample bottle.
- 4.4 Place additional bubble wrap and/or styrofoam pellet packing material throughout the voids between sample containers within each cooler.
- 4.5 Place ice or cold packs in heavy duty zip-loc type plastic bags, close the bags, and distribute such packages over the top of the samples.
- 4.6 Add additional bubble wrap/styrofoam pellets to fill the balance of the cooler or container.
- 4.7 Obtain two pieces of chain of custody tape as shown in Figure 2 and enter the custody tape numbers in the appropriate place on the chain of custody form. Sign and date the chain of custody tape.

- 4.8 To complete the chain of custody form enter the type of analysis required for each sample, by container, under the "ANALYSES" section. Under the specific analysis enter the quantity/volume of sample collected for each corresponding analysis.

If shipping the samples where travel by air or other public transportation is to be undertaken, sign the chain of custody record thereby relinquishing custody of the samples. Relinquishing custody should only be performed when directly transmitting custody to a receiving party or when transmitting to a shipper for subsequent receipt by the analytical laboratory. Shippers should not be asked to sign chain of custody records.

- 4.9 Remove the back carbon copy from the chain of custody record and retain with other field notes. Place the remaining copies in a zip-lock type plastic bag and place the bag on the top of the contents within the cooler or shipping container.
- 4.10 Close the top or lid of the cooler or shipping container and with another person rotate/shake the container to verify that the contents are packed so that they do not move. Improve the packaging if needed and reclose.

When travelling with samples by automobile, and where periodic changes of ice are required, the cooler should only be temporarily closed so that reopening is simple. In these cases, chain of custody will be maintained by the person transporting the sample and chain of custody tape will not be used.

- 4.11 Place the chain of custody tape at two different locations on the cooler or container lid and overlap with transparent packaging tape.
- 4.12 Packaging tape should be placed entirely around the sample shipment containers. A minimum of one to two full rotations of packaging tape will be placed at at least two places on the cooler. Shake the cooler again to verify that the sample containers are well packed.
- 4.13 If shipment is required, transport the cooler to an overnight express package terminal. Obtain copies of all shipment records as provided by the shipper.
- 4.14 If the samples are to travel as luggage, check with regular baggage.

0908J

STANDARD OPERATING PROCEDURE

Page 4 6

Title: Packaging and Shipment of Samples

Date 1st Qtr. 1984
Number SOP 7510
Revision

4.15 Upon receipt of the samples, the analytical laboratory will open the cooler or shipping container and sign as "received for laboratory" each chain of custody form. The laboratory will verify that the chain of custody tape has not been broken previously and that the chain of custody tape number corresponds with the number on the chain of custody record. The analytical laboratory will then forward the back copy of the chain of custody record to the sample collector to indicate that sample transmittal is complete.

5.0 Documentation

As discussed in Section 4.0 the documentation for supporting the sample packaging and shipping will consist of chain of custody records and shipper's records. In addition a description of sample packaging procedures will be written in the field log book. All documentation will be retained in the project files following project completion.

Client/Project Name			Project Location			<div style="text-align: center;">ANALYSES</div>						
Project No			Field Logbook No									
Sampler: (Signature)			Chain of Custody Tape No									
Sample No / Identification	Date	Time	Lab Sample Number	Type of Sample							REMARKS	
Relinquished by: (Signature)					Date	Time	Received by (Signature)				Date	Time
Relinquished by: (Signature)					Date	Time	Received by (Signature)				Date	Time
Relinquished by: (Signature)					Date	Time	Received for Laboratory (Signature)				Date	Time
Sample Disposal Method					Disposed of by (Signature)						Date	Time
SAMPLE COLLECTOR Environmental Research and Technology, Inc 696 Virginia Road Concord, MA 01742 617-369-8910					ANALYTICAL LABORATORY <div style="text-align: right;"> ERT No 1661 </div>							

ERT

Date _____

Sig. _____

Nº 30432

Figure 2

obtained should be reported with the sample results.

14. Method Performance

14.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.¹ The MDL concentration listed in Table 1 was obtained using reagent water.¹⁴ The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

14.2 This method was tested by 11 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 0.02 to 0.20 µg/L.¹⁵ Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 3.

References

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11. Provost, L. P., and Elder, R. S., "Interpretation of Percent Recovery Data," *American Laboratory*, 15, 58-63 (1983). (The value 2.44 used in the equation in Section 8.3.3 is two times the value 1.22 derived in this report.)

12. ASTM Annual Book of Standards, Part 31, D3370-78, "Standard Practices for Sampling Water," American Society for Testing and Materials, Philadelphia.

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Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.

14. Wong, A.S. et al. "The Determination of 2,3,7,8-TCDD in Industrial and Municipal Wastewaters, Method 613, Part 1—Development and Detection Limits," G. Choudhary, L. Keith, and C. Ruppe, ed., Butterworth Inc., (1983).

15. "EPA Method Validation Study 23, Method 613 (2,3,7,8-Tetrachlorodibenzo-p-dioxin)," Report for EPA Contract 68-03-2863 (In preparation).

TABLE 1.—Chromatographic Conditions and Method Detection Limit

Parameter	Retention time (min)	Method detection limit (µg/L)
2,3,7,8-TCDD	13.1	0.002

Column conditions: SP-2330 coated on a 60 m long x 0.25 mm ID glass column with hydrogen carrier gas at 40 cm/sec linear velocity, splitless injection using tetradecane. Column temperature held isothermal at 200°C for 1 min, then programmed at 8°C/min to 250°C and held. Use of helium carrier gas will approximately double the retention time.

TABLE 2.—GC Acceptance Criteria—Method 613

Parameter	Test conc (µg/L)	Limit for s (µg/L)	Range for X (µg/L)	Range for P, P _r (%)
2,3,7,8-TCDD	0.100	0.0276	0.0523-0.1226	45-129

s = Standard deviation of four recovery measurements, in µg/L (Section 8.2.4).

X = Average recovery for four recovery measurements, in µg/L (Section 8.2.4).

P, P_r = Percent recovery measured (Section 8.3.2, Section 8.4.2).

Notes.—These criteria are based directly upon the method performance data in Table 3. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 3.

TABLE 3.—METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 613

Parameter	Accuracy as recovery, A (µg/L)	Single analyst precision, s, (µg/L)	Overall precision, S (µg/L)
2,3,7,8 TCDD	0.86C + 0.00145	0.13R + 0.00129	0.19R + 0.00028

C = Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L.

s = Expected single analyst standard deviation of measurements at an average concentration found of X, in µg/L.

S = Expected interlaboratory standard deviation of measurements at an average concentration found of X, in µg/L.

C = True value for the concentration, in µg/L.

X = Average recovery found for measurements of samples containing a concentration of C, in µg/L.

Method 624—Purgeables

1. Scope and Application

1.1 This method covers the determination of a number of purgeable organics. The following parameters may be determined by this method:

Parameter	STORET No.	CAS No.
Benzene	34030	71-43-2
Bromochloromethane	32101	75-27-4
Bromotoluene	32104	75-25-2
Bromomethane	34413	74-83-9
Carbon tetrachloride	32102	56-23-5
Chlorobenzene	34301	108-90-7
Chloroethane	34311	75-00-3
1-Chloroethylmethyl ether	34576	110-75-6
Chloroform	32106	67-66-3

Parameter	STORET No.	CAS No.
Chloromethane	34418	74-87-3
Dibromochloromethane	32105	124-48-1
1,2-Dichlorobenzene	34538	95-50-1
1,3-Dichlorobenzene	34566	541-73-1
1,4-Dichlorobenzene	34571	106-46-7
1,1-Dichloroethane	34496	75-34-3
1,2-Dichloroethane	34531	107-08-2
1,1-Dichloroethane	34501	75-35-4
trans-1,2-Dichloroethane	34546	156-60-5
1,2-Dichloropropane	34541	78-67-5
cis-1,3-Dichloropropane	34704	10061-01-5
trans-1,3-Dichloropropane	34699	10061-02-6
Ethyl benzene	34371	100-41-4
Methylene chloride	34423	75-09-2
1,1,2,2-Tetrachloroethane	34516	79-34-5
Tetrachloroethane	34475	127-18-4
Toluene	34010	108-88-3
1,1,1-Trichloroethane	34506	71-55-6
1,1,2-Trichloroethane	34511	79-00-5

Parameter	STORET No.	CAS No.
Trichloroethane	39180	78-01-6
Trichlorofluoromethane	34488	75-69-4
Vinyl chloride	39175	75-01-4

1.2 The method may be extended to screen samples for acrolein (STORET No. 34210, CAS No. 107-02-8) and acrylonitrile (STORET No. 34215, CAS No. 107-13-1), however, the preferred method for these two compounds is Method 603.

1.3 This is a purge and trap gas chromatography/mass spectrometry (GC/MS) method applicable to the determination of the compounds listed above in municipal

and industrial discharges as provided under 40 CFR 136.1.

1.4 The method detection limit (MDL, defined in Section 14.1)¹ for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.5 Any modification to this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5. Depending upon the nature of the modification and the extent of intended use, the applicant may be required to demonstrate that the modifications will produce equivalent results when applied to relevant wastewaters.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the operation of a purge and trap system and a gas chromatograph/mass spectrometer and in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 An inert gas is bubbled through a 5-mL water sample contained in a specially-designed purging chamber at ambient temperature. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent trap where the purgeables are trapped. After purging is completed, the trap is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeables which are then detected with a mass spectrometer.^{2,3}

3. Interferences

3.1 Impurities in the purge gas, organic compounds outgassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3. The use of non-Teflon plastic tubing, non-Teflon thread sealants, or flow controllers with rubber components in the purge and trap system should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during shipment and storage. A field reagent blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry-over, the purging device and sample syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it should be followed by an

analysis of reagent water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high purgeable levels, it may be necessary to wash the purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105 °C oven between analyses. The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified^{4,5} for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform, 1,4-dichlorobenzene, and vinyl chloride. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete sampling.

5.1.1 Vial—25-mL capacity or larger, equipped with a screw cap with a hole in the center (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105 °C before use.

5.1.2 Septum—Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105 °C for 1 h before use.

5.2 Purge and trap system—The purge and trap system consists of three separate pieces of equipment: a purging device, trap, and desorber. Several complete systems are now commercially available.

5.2.1 The purging device must be designed to accept 5-mL samples with a water column at least 3 cm deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The purging device illustrated in Figure 1 meets these design criteria.

5.2.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in. The trap must be packed to contain the

following minimum lengths of adsorbents: 1.0 cm of methyl silicone coated packing (Section 6.3.2), 15 cm of 2,6-diphenylene oxide polymer (Section 6.3.1), and 8 cm of silica gel (Section 6.3.3). The minimum specifications for the trap are illustrated in Figure 2.

5.2.3 The desorber should be capable of rapidly heating the trap to 180 °C. The polymer section of the trap should not be heated higher than 180 °C and the remaining sections should not exceed 200 °C. The desorber illustrated in Figure 2 meets these design criteria.

5.2.4 The purge and trap system may be assembled as a separate unit or be coupled to a gas chromatograph as illustrated in Figures 3 and 4.

5.3 GC/MS system:

5.3.1 Gas chromatograph—An analytical system complete with a temperature programmable gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, and gases.

5.3.2 Column—6 ft long x 0.1 in ID stainless steel or glass, packed with 1% SP-1000 on Carbowax B (60/80 mesh) or equivalent. This column was used to develop the method performance statements in Section 14. Guidelines for the use of alternate column packings are provided in Section 11.1.

5.3.3 Mass spectrometer—Capable of scanning from 20 to 260 amu every 7 s or less, utilizing 70 V (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the criteria in Table 2 when 50 ng of 4-bromofluorobenzene (BFB) is injected through the GC inlet.

5.3.4 GC/MS interface—Any GC to MS interface that gives acceptable calibration points at 50 ng or less per injection for each of the parameters of interest and achieves all acceptable performance criteria (Section 10) may be used. GC to MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

5.3.5 Data system—A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for specific m/z (masses) and plotting such m/z abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

5.4 Syringes—5-mL, glass hypodermic with Luerlok tip (two each), if applicable to the purging device.

5.5 Micro syringes—25-μL, 0.006 in. ID needle.

5.6 Syringe valve—2-way, with Luer ends (three each).

5.7 Syringe—5-mL, gas-tight with shut-off valve.

5.8 Bottle—15-mL, screw-cap, with Teflon cap liner.

5.9 Balance—Analytical, capable of accurately weighing 0.0001 g.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.1.1 Reagent water can be generated by passing tap water through a carbon filter bed containing about 1 lb of activated carbon (Filtrosorb-300, Calgon Corp., or equivalent).

6.1.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

6.1.3 Reagent water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90 °C, bubble a contaminant-free inert gas through the water for 1 h. While still hot, transfer the water to a narrow mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

6.2 Sodium thiosulfate—(ACS) Granular.

6.3 Trap materials:

6.3.1 2,6-Diphenylene oxide polymer—Tenax, (60/80 mesh), chromatographic grade or equivalent.

6.3.2 Methyl silicone packing—3% OV-1 on Chromosorb-W (60/80 mesh) or equivalent.

6.3.3 Silica gel—35/60 mesh, Davison, grade-15 or equivalent.

6.4 Methanol—Pesticide quality or equivalent.

6.5 Stock standard solutions—Stock standard solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol using assayed liquids or gases as appropriate. Because of the toxicity of some of the compounds, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be used when the analyst handles high concentrations of such materials.

6.5.1 Place about 9.8 mL of methanol into a 10-mL ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

6.5.2 Add the assayed reference material:

6.5.2.1 Liquids—Using a 100-μL syringe, immediately add two or more drops of assayed reference material to the flask, then reweigh. Be sure that the drops fall directly into the alcohol without contacting the neck of the flask.

6.5.2.2 Gases—To prepare standards for any of the four halocarbons that boil below 30 °C (bromomethane, chloroethane, chloromethane, and vinyl chloride), fill a 5-mL valved gas-tight syringe with the reference standard to the 5.0-mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid (the heavy gas will rapidly dissolve in the methanol).

6.5.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in μg/μL from the net gain in weight. When compound purity is assayed to be 98% or greater, the weight may be used without correction to

calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

6.5.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store, with minimal headspace, at -10 to -20 °C and protect from light.

6.5.5 Prepare fresh standards weekly for the four gases and 2-chloroethylvinyl ether. All other standards must be replaced after one month, or sooner if comparison with check standards indicates a problem.

6.6 Secondary dilution standards—Using stock solutions, prepare secondary dilution standards in methanol that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Section 7.3 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.7 Surrogate standard spiking solution—Select a minimum of three surrogate compounds from Table 3. Prepare stock standard solutions for each surrogate standard in methanol as described in Section 6.5. Prepare a surrogate standard spiking solution from these stock standards at a concentration of 15 μg/mL in water. Store the solutions at 4 °C in Teflon-sealed glass containers with a minimum of headspace. The solutions should be checked frequently for stability. The addition of 10 μL of this solution of 5 mL of sample or standard is equivalent to a concentration of 30 μg/L of each surrogate standard.

6.8 BFB Standard—Prepare a 25 μg/mL solution of BFB in methanol.

6.9 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Assemble a purge and trap system that meets the specifications in Section 5.2. Condition the trap overnight at 180 °C by backflushing with an inert gas flow of at least 20 mL/min. Condition the trap for 10 min once daily prior to use.

7.2 Connect the purge and trap system to a gas chromatograph. The gas chromatograph must be operated using temperature and flow rate conditions equivalent to those given in Table 1.

7.3 Internal standard calibration procedure—To use this approach, the analyst must select three or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Some recommended internal standards are listed in Table 3.

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter by carefully adding 20.0 μL of one or more secondary dilution standards to 50, 250, or 500 mL of reagent water. A 25-μL

syringe with a 0.008 in. ID needle should be used for this operation. One of the calibration standards should be at a concentration near, but above, the MDL (Table 1) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system. These aqueous standards can be stored up to 24 h, if held in sealed vials with zero headspace as described in Section 9.2. If not so stored, they must be discarded after 1 h.

7.3.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 6.5 and 6.6. It is recommended that the secondary dilution standard be prepared at a concentration of 15 μg/mL of each internal standard compound. The addition of 10 μL of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 μg/L.

7.3.3 Analyze each calibration standard according to Section 11, adding 10 μL of internal standard spiking solution directly to the syringe (Section 11.4). Tabulate the area response of the characteristic m/z against concentration for each compound and internal standard, and calculate response factors (RF) for each compound using Equation 1.

Equation 1.

$$RF = \frac{(A_s)(C_{in})}{(A_{in})(C_s)}$$

where:

A_s = Area of the characteristic m/z for the parameter to be measured.

A_{in} = Area of the characteristic m/z for the internal standard.

C_{in} = Concentration of the internal standard.

C_s = Concentration of the parameter to be measured.

If the RF value over the working range is a constant (<35% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{in} , vs. RF.

7.4 The working calibration curve or RF must be verified on each working day by the measurement of a QC check sample.

7.4.1 Prepare the QC check sample as described in Section 8.2.2.

7.4.2 Analyze the QC check sample according to the method beginning in Section 10.

7.4.3 For each parameter, compare the response (Q) with the corresponding calibration acceptance criteria found in Table 5. If the responses for all parameters of interest fall within the designated ranges, analysis of actual samples can begin. If any individual Q falls outside the range, proceed according to Section 7.4.4.

Note.—The large number of parameters in Table 5 present a substantial probability that one or more will not meet the calibration

acceptance criteria when all parameters are analyzed.

7.4.4 Repeat the test only for those parameters that failed to meet the calibration acceptance criteria. If the response for a parameter does not fall within the range in this second test, a new calibration curve or RF must be prepared for that parameter according to Section 7.3.

8 Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.1 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Section 11.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Each day, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system are under control.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 5% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 5% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must spike all samples with surrogate standards to monitor continuing laboratory performance. This procedure is described in Section 8.5.

8.1.7 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.6.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each parameter of interest at a concentration of 10

µg/mL in methanol. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Prepare a QC check sample to contain 20 µg/L of each parameter by adding 200 µL of QC-check sample concentrate to 100 mL of reagent water.

8.2.3 Analyze four 5-mL aliquots of the well-mixed QC check sample according to the method beginning in Section 10.

8.2.4 Calculate the average recovery (\bar{X}) in µg/L and the standard deviation of the recovery (s) in µg/L for each parameter of interest using the four results.

8.2.5 For each parameter compare s and \bar{X} with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 5. If s and \bar{X} for all parameters of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual \bar{X} falls outside the range for accuracy, the system performance is unacceptable for that parameter.

Note.—The large number of parameters in Table 5 present a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed.

8.2.6 When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.2.6.1 or 8.2.6.2.

8.2.6.1 Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.3.

8.2.6.2 Beginning with Section 8.2.3, repeat the test only for those parameters that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.2.3.

8.3 The laboratory must, on an ongoing basis, spike at least 5% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing 1 to 20 samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at 20 µg/L or 1 to 5 times

higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.2 Analyze one 5-mL sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second 5-mL sample aliquot with 10 µL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as $100(A-B)/T$, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 5. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 20 µg/L, the analyst must use either the QC acceptance criteria in Table 5, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) calculate accuracy (X') using the equation in Table 6, substituting the spike concentration (T) for C ; (2) calculate overall precision (S') using the equation in Table 6, substituting X' for \bar{X} ; (3) calculate the range for recovery at the spike concentration as $(100 X'/T) (\pm 2.44(100 S'/T)\%)$.

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

Note.—The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of parameters in Table 5 must be measured in the sample in Section 8.3, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spiked sample.

8.4.1 Prepare the QC check standard by adding 10 µL of QC check sample concentrate (Sections 8.2.1 or 8.3.2) to 5 mL of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_2) as $100(A/T)\%$, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_2) for each parameter with the corresponding QC acceptance criteria found in Table 5.

Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter fails outside the designated range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As a quality control check, the laboratory must spike all samples with the surrogate standard spiking solutions as described in Section 11.4, and calculate the percent recovery of each surrogate compound.

8.6 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery (\bar{P}) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{P} - 2s_p$ to $\bar{P} + 2s_p$. If $\bar{P} = 90\%$ and $s_p = 10\%$, for example, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each parameter a regular basis (e.g., after each five to ten new accuracy measurements).

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 All samples must be iced or refrigerated from the time of collection until analysis. If the sample contains residual chlorine, add sodium thiosulfate preservative (10 mL/40 mL is sufficient for up to 5 ppm Cl₂) to the empty sample bottle just prior to shipping to the sampling site. EPA Methods 801.4 and 801.5 may be used for measurement of residual chlorine.⁸ Field test kits are available for this purpose.

9.2 Grab samples must be collected in glass containers having a total volume of at least 25 mL. Fill the sample bottle just to overflowing in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottle so that no air bubbles are entrapped in it. If preservative has been added, shake vigorously for 1 min. Maintain the hermetic seal on the sample bottle until time of analysis.

9.3 Experimental evidence indicates that many aromatic compounds, notably benzene, toluene, and ethyl benzene are susceptible to rapid biological degradation under certain environmental conditions.⁹ Refrigeration alone may not be adequate to preserve these compounds in wastewaters for more than seven days. For this reason, a separate sample should be collected, acidified, and analyzed when these aromatics are to be

determined. Collect about 500 mL of sample in a clean container. Adjust the pH of the sample to about 2 by adding 1 + 1 HCl while stirring vigorously. Check pH with narrow range (1.4 to 2.8) pH paper. Fill a sample container as described in Section 9.2.

9.4 All samples must be analyzed within 14 days of collection.⁹

10. Daily GC/MS Performance Tests

10.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria are achieved for BFB.⁹ The performance test must be passed before any samples, blanks, or standards are analyzed, unless the instrument has met the DF-PP test described in Method 625 earlier in the day.¹⁰

10.2 These performance tests require the following instrumental parameters:

Electron Energy: 70 V (nominal)

Mass Range: 20 to 260 amu

Scan Time: To give at least 5 scans per peak but not to exceed 7 s per scan.

10.3 At the beginning of each day, inject 2 μ L of BFB solution directly on the column. Alternatively, add 2 μ L of BFB solution to 5.0 mL of reagent water or standard solution and analyze the solution according to section 11. Obtain a background-corrected mass spectrum of BFB and confirm that all the key m/z criteria in Table 2 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved.

11. Sample Purging and Gas Chromatography

11.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times and MDL that can be achieved under these conditions. An example of the separations achieved by this column is shown in Figure 5. Other packed columns or chromatographic conditions may be used if the requirements of Section 8.2 are met.

11.2 After achieving the key m/z abundance criteria in Section 10, calibrate the system daily as described in Section 7.

11.3 Adjust the purge gas (helium) flow rate to 40 mL/min. Attach the trap inlet to the purging device, and set the purge and trap system to purge (Figure 3). Open the syringe valve located on the purging device sample introduction needle.

11.4 Allow the sample to come to ambient temperature prior to introducing it into the syringe. Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data. Add 10.0 μ L of the surrogate spiking solution (Section 6.7) and 10.0 μ L of the internal standard spiking solution (Section 7.3.2) through the valve bore, then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution.

11.5 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

11.6 Close both valves and purge the sample for 11.0 \pm 0.1 min at ambient temperature.

11.7 After the 11-min purge time, attach the trap to the chromatograph, adjust the purge and trap system to the desorb mode (Figure 4), and begin to temperature program the gas chromatograph. Introduce the trapped materials to the GC column by rapidly heating the trap to 180 °C while backflushing the trap with an inert gas between 20 and 60 mL/min for 4 min. If rapid heating of the trap cannot be achieved, the GC column must be used as a secondary trap by cooling it to 30 °C (subambient temperature, if problems persist) instead of the initial program temperature of 45 °C.

11.8 While the trap is being desorbed into the gas chromatograph, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 5-mL flushes of reagent water.

11.9 After desorbing the sample for 4 min, recondition the trap by returning the purge and trap system to the purge mode. Wait 15 s then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180 °C. After approximately 7 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

11.10 If the response for any m/z exceeds the working range of the system, prepare a dilution of the sample with reagent water from the aliquot in the second syringe and reanalyze.

12. Qualitative Identification

12.1 Obtain EICs for the primary m/z (Table 4) and at least two secondary masses for each parameter of interest. The following criteria must be met to make a qualitative identification.

12.1.1 The characteristic masses of each parameter of interest must appear in the same or within one scan of each other.

12.1.2 The retention time must fall within ± 30 s of the retention time of the authentic compound.

12.1.3 The relative peak heights of the three characteristic masses in the EICs must fall within $\pm 20\%$ of the relative intensities of these masses in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library.

12.2 Structural isomers that have very similar mass spectra and less than 30 s difference in retention time, can be explicitly identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

13. Calculations

13.1 When a parameter has been identified, the quantitation of that parameter should be based on the integrated abundance

from the EICP of the primary characteristic m/z given in Table 4. If the sample produces an interference for the primary m/z , use a secondary characteristic m/z quantitate.

Calculate the concentration in the sample using the response factor (RF) determined in Section 7.3.3 and Equation 2.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(C_{is})}{(A_{is})(\text{RF})}$$

where:

A_s = Area of the characteristic m/z for the parameter or surrogate standard to be measured.

A_{is} = Area of the characteristic m/z for the internal standard.

C_{is} = Concentration of the internal standard.

13.2 Report results in $\mu\text{g/L}$ without correction for recovery data. All QC data obtained should be reported with the sample results.

14. Method Performance

14.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

14.2 This method was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 3–600 $\mu\text{g/L}$. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 5.

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TABLE 1.—CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention time (min)	Method detection limit ($\mu\text{g/L}$)
Chloromethane	2.3	nd
Bromomethane	3.1	nd
Vinyl chloride	3.8	nd
Chloroethane	4.6	nd
Methylene chloride	6.4	2.6
Trichlorofluoromethane	8.3	nd
1,1-Dichloroethene	9.0	2.8
1,1-Dichloroethane	10.1	4.7
trans-1,2-Dichloroethene	10.8	1.6
Chloroform	11.4	1.6
1,2-Dichloroethane	12.1	2.8
1,1,1-Trichloroethane	13.4	3.8
Carbon tetrachloride	13.7	2.8
Bromodichloromethane	14.3	2.2
1,2-Dichloropropane	15.7	6.0
cis-1,3-Dichloropropene	15.9	5.0
Trichloroethene	16.5	1.9
Benzene	17.0	4.4
Dibromochloromethane	17.1	3.1
1,1,2-Trichloroethane	17.2	5.0
trans-1,3-Dichloropropene	17.2	nd
2-Chloroethylvinyl ether	18.6	nd
Bromoform	19.8	4.7
1,1,2,2-Tetrachloroethane	22.1	6.9
Tetrachloroethene	22.2	4.1

TABLE 1.—CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS—Continued

Parameter	Retention time (min)	Method detection limit ($\mu\text{g/L}$)
Toluene	23.5	6.0
Chlorobenzene	24.6	6.0
Ethyl benzene	26.4	7.2
1,3-Dichlorobenzene	33.9	nd
1,2-Dichlorobenzene	35.0	nd
1,4-Dichlorobenzene	35.4	nd

Column conditions: Carbowax B (60/80 mesh) coated with 1% SP-1000 packed in a 6 ft by 0.1 in. ID glass column with helium carrier gas at 30 mL/min flow rate. Column temperature held at 45°C for 3 min then programmed at 8°C/min to 220°C and held for 15 min. nd=not determined.

TABLE 2.—BFB KEY m/z ABUNDANCE CRITERIA

Mass	m/z Abundance criteria
50	15 to 40% of mass 95
75	20 to 60% of mass 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95
173	<2% of mass 174
174	>50% of mass 95
175	5 to 9% of mass 174
176	>95% but < 101% of mass 174
177	5 to 9% of mass 176

TABLE 3.—SUGGESTED SURROGATE AND INTERNAL STANDARDS

Compound	Retention time (min)	Primary m/z	Secondary masses
Benzene d-6	17.0	84	
4-Bromofluorobenzene	28.3	95	174, 176
1,2-Dichloroethane d-4	12.1	102	
1,4-Difluorobenzene	19.8	114	63, 80
Ethylbenzene d-5	26.4	111	
Ethylbenzene d-10	26.4	93	
Fluorobenzene	18.4	96	70
Perfluorobenzene	23.5	168	
Bromochloromethane	9.3	128	49, 130, 51
2-Bromo-1-chloropropane	19.2	77	79, 156
1,4-Dichlorobutane	25.8	55	90, 92

*For chromatographic conditions, see Table 1

TABLE 4.—CHARACTERISTIC MASSES FOR PURGEABLE ORGANICS

Parameter	Primary	Secondary
Chloromethane	50	52
Bromomethane	94	96
Vinyl chloride	62	64
Chloroethane	64	66
Methylene chloride	84	49, 51 and 86
Trichlorofluoromethane	101	103
1,1-Dichloroethene	96	61 and 98
1,1-Dichloroethane	63	85, 93, 35, 93, and 100
trans-1,2-Dichloroethene	96	61 and 98
Chloroform	83	85
1,2-Dichloroethane	98	62, 64, and 100
1,1,1-Trichloroethane	97	99, 117, and 119
Carbon tetrachloride	117	119 and 121
Bromodichloromethane	127	83, 85, and 129
1,2-Dichloropropane	112	83, 65, and 114
trans-1,3-Dichloropropene	75	77
Trichloroethene	130	95, 97, and 132
Benzene	78	
Dibromochloromethane	127	129, 208 and 206
1,1,2-Trichloroethane	97	83, 95, 96, 132, and 134
cis-1,3-Dichloropropene	75	77
2-Chloroethylvinyl ether	106	63 and 85

TABLE 4.—CHARACTERISTIC MASSES FOR
PURGEABLE ORGANICS—Continued

Parameter	Primary	Secondary
Bromotom.	173	171, 175, 250 252, 254, and 256
1,1,2,2-Tetrachloroethane	168	83, 85 131 133 and 166

TABLE 4.—CHARACTERISTIC MASSES FOR
PURGEABLE ORGANICS—Continued

Parameter	Primary	Secondary
Tetrachloroethene	164	129, 131, and 168
Toluene	92	91
Chlorobenzene	112	114
Ethyl benzene	106	91.

TABLE 4.—CHARACTERISTIC MASSES FOR
PURGEABLE ORGANICS—Continued

Parameter	Primary	Secondary
1,3-Dichlorobenzene	146	146 and 113
1,2-Dichlorobenzene	146	146 and 113
1,4-Dichlorobenzene	146	146 and 113

TABLE 5.—CALIBRATION AND QC ACCEPTANCE CRITERIA—METHOD 624^a

Parameter	Range for Q (μ /g/L)	Limit for s (μ /g/L)	Range for \bar{X} (μ /g/L)	Range for P, P _r (%)
Benzene	12.8–27.2	6.9	15.2–28.0	37–151
Bromodichloromethane	13.1–26.9	6.4	10.1–28.0	35–155
Bromotom.	14.2–25.8	5.4	11.4–31.1	45–169
Bromomethane	2.8–37.2	17.9	0–41.2	0–242
Carbon tetrachloride	14.6–25.4	5.2	17.2–23.5	70–140
Chlorobenzene	13.2–26.8	6.3	16.4–27.4	37–160
Chloroethane	7.6–32.4	11.4	8.4–40.4	14–230
2-Chloroethylvinyl ether	0–44.8	25.9	0–50.4	0–305
Chlorotom.	13.5–28.5	6.1	13.7–24.2	51–138
Chloromethane	0–40.8	19.8	0–45.9	0–273
Dibromochloromethane	13.5–26.5	6.1	13.8–26.6	53–149
1,2-Dichlorobenzene	12.6–27.4	7.1	11.8–34.7	18–190
1,3-Dichlorobenzene	14.6–25.4	5.5	17.0–28.8	59–156
1,4-Dichlorobenzene	12.6–27.4	7.1	11.8–34.7	18–190
1,1-Dichloroethane	14.5–25.5	5.1	14.2–26.5	59–155
1,2-Dichloroethane	13.6–26.4	6.0	14.3–27.4	49–155
1,1-Dichloroethene	10.1–29.9	9.1	3.7–42.3	0–234
trans-1,2-Dichloroethene	13.9–26.1	5.7	13.8–26.5	54–158
1,2-Dichloropropane	6.8–33.2	13.8	3.8–35.2	0–210
cis-1,3-Dichloropropene	4.8–35.2	15.6	1.0–39.0	0–227
trans-1,3-Dichloropropene	10.0–30.0	10.4	7.6–32.4	17–183
Ethyl benzene	11.8–28.2	7.5	17.4–26.7	37–162
Methylene chloride	12.1–27.9	7.4	0–41.0	0–221
1,1,2,2-Tetrachloroethane	12.1–27.9	7.4	13.5–27.2	46–157
Tetrachloroethene	14.7–25.3	5.0	17.0–26.6	64–148
Toluene	14.9–25.1	4.8	16.6–26.7	47–162
1,1,1-Trichloroethane	15.0–25.0	4.8	13.7–30.1	52–162
1,1,2-Trichloroethane	14.2–25.8	5.5	14.3–27.1	52–150
Trichloroethane	13.3–26.7	6.6	18.6–27.6	71–157
Trichlorofluoromethane	9.8–30.4	10.0	8.9–31.5	17–181
Vinyl chloride	0.8–39.2	20.0	0–43.5	0–251

Q = Concentration measured in QC check sample, in μ g/L (Section 7.5.3)s = Standard deviation of four recovery measurements, in μ g/L (Section 8.2.4) \bar{X} = Average recovery of four recovery measurements, in μ g/L (Section 8.2.4)P, P_r = Percent recovery measured, (Section 8.3.2, Section 8.4.2).

D = Detected, result must be greater than zero

^aCriteria were calculated assuming a QC check sample concentration of 20 μ g/L.

NOTE—These criteria are based directly upon the method performance data in Table 6. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 6.

TABLE 6.—METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 624

Parameter	Accuracy, as recovery, X (μ g/L)	Single analyst precision, s, (μ g/L)	Overall precision, S (μ g/L)
Benzene	0.93C+2.00	0.26 \bar{X} –1.74	0.25 \bar{X} –1.33
Bromodichloromethane	1.03C–1.58	0.15 \bar{X} +0.59	0.20 \bar{X} +1.13
Bromotom.	1.18C–2.35	0.12 \bar{X} +0.34	0.17 \bar{X} +1.38
Bromomethane ^a	1.00C	0.43 \bar{X}	0.58 \bar{X}
Carbon tetrachloride	1.10C–1.68	0.12 \bar{X} +0.25	0.11 \bar{X} +0.37
Chlorobenzene	0.98C+2.28	0.16 \bar{X} –0.09	0.26 \bar{X} –1.92
Chloroethane	1.18C+0.81	0.14 \bar{X} +2.78	0.29 \bar{X} +1.75
2-Chloroethylvinyl ether ^a	1.00C	0.62 \bar{X}	0.84 \bar{X}
Chlorotom.	0.93C+0.33	0.16 \bar{X} +0.22	0.18 \bar{X} –0.16
Chloromethane	1.03C–1.81	0.37 \bar{X} +2.14	0.58 \bar{X} +0.43
Dibromochloromethane	1.01C–0.03	0.17 \bar{X} –0.18	0.17 \bar{X} +0.49
1,2-Dichlorobenzene ^a	0.94C+4.47	0.22 \bar{X} –1.45	0.30 \bar{X} –1.20
1,3-Dichlorobenzene	1.06C+1.68	0.14 \bar{X} –0.48	0.18 \bar{X} –0.82
1,4-Dichlorobenzene ^a	0.94C+4.47	0.22 \bar{X} –1.45	0.30 \bar{X} –1.20
1,1-Dichloroethane	1.05C+0.36	0.13 \bar{X} –0.05	0.16 \bar{X} +0.47
1,2-Dichloroethane	1.02C+0.45	0.17 \bar{X} –0.32	0.21 \bar{X} –0.38
1,1-Dichloroethene	1.12C+0.61	0.17 \bar{X} +1.06	0.43 \bar{X} –0.22
trans-1,2-Dichloroethene	1.05C+0.03	0.14 \bar{X} +0.09	0.19 \bar{X} –0.17
1,2-Dichloropropane ^a	1.00C	0.33 \bar{X}	0.45 \bar{X}
cis-1,3-Dichloropropene ^a	1.00C	0.38 \bar{X}	0.52 \bar{X}
trans-1,3-Dichloropropene ^a	1.00C	0.25 \bar{X}	0.34 \bar{X}
Ethyl benzene	0.98C+2.48	0.14 \bar{X} +1.00	0.26 \bar{X} –1.72
Methylene chloride	0.87C+1.88	0.15 \bar{X} +1.07	0.32 \bar{X} +4.00
1,1,2,2-Tetrachloroethane	0.93C+1.78	0.16 \bar{X} +0.69	0.20 \bar{X} +0.41

TABLE 6.—METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 624—Continued

Parameter	Accuracy, as recovery \bar{X} ($\mu\text{g/L}$)	Single analyst precision, s_x ($\mu\text{g/L}$)	Overall precision, S ($\mu\text{g/L}$)
Tetrachloroethene	105C-0.00	0.13 \bar{X} -0.18	0.15 \bar{X} -0.45
Toluene	0.98C-2.03	0.13 \bar{X} -0.71	0.22 \bar{X} -1.71
1,1,1-Trichloroethane	103C-0.73	0.12 \bar{X} -0.15	0.21 \bar{X} -0.39
1,1,2-Trichloroethane	0.95-1.71	0.14 \bar{X} -0.02	0.18 \bar{X} -0.00
Trichloroethene	101C-2.27	0.13 \bar{X} -0.36	0.12 \bar{X} -0.59
Trichlorofluoromethane	0.99C-0.39	0.33 \bar{X} -1.48	0.34 \bar{X} -0.39
Vinyl chloride	100C	0.18 \bar{X}	0.05 \bar{X}

\bar{X} = Expected recovery for one or more measurements of a sample containing a concentration of C, in $\mu\text{g/L}$.

S_x = Expected single analyst standard deviation of measurements at an average concentration found at \bar{X} , in $\mu\text{g/L}$.

S = Expected interlaboratory standard deviation of measurements at an average concentration found at \bar{X} , in $\mu\text{g/L}$.

C = True value for the concentration, in $\mu\text{g/L}$.

\bar{X} = Average recovery found for measurements of samples containing a concentration of C, in $\mu\text{g/L}$.

^a Estimates based upon the performance in a single laboratory.¹³

^b Due to chromatographic resolution problems, performance statements for these isomers are based upon the sums of their concentrations.

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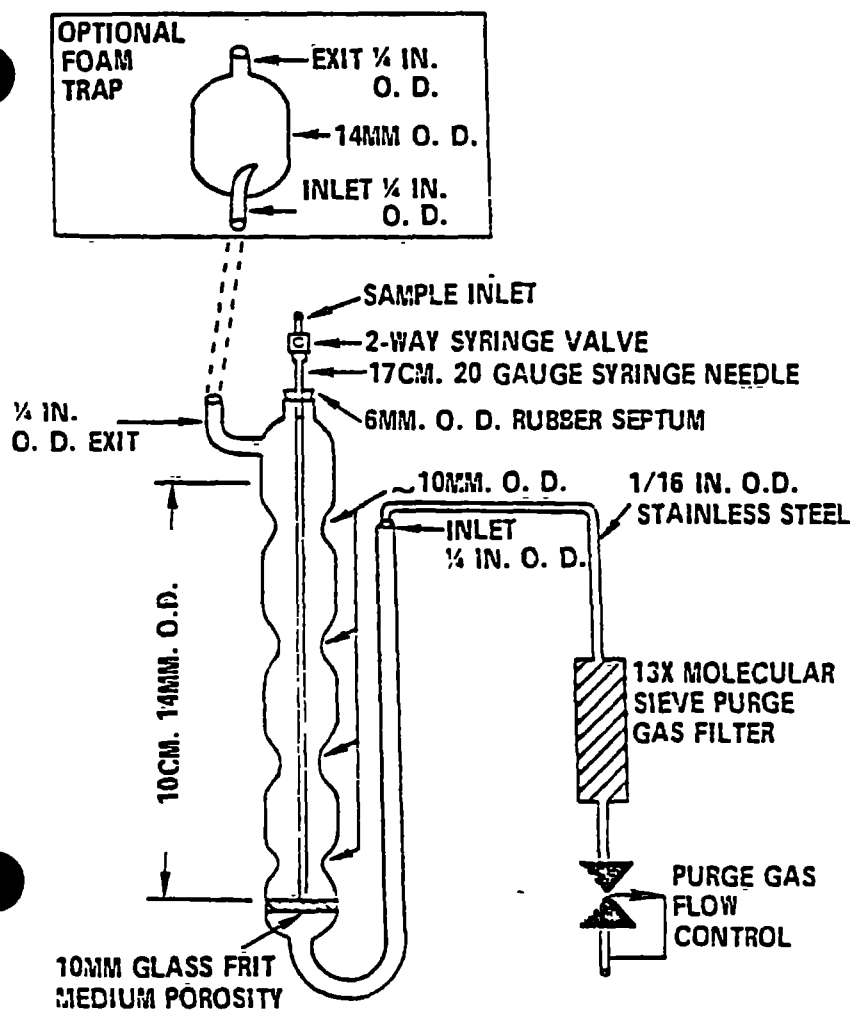


Figure 1. Purging device.

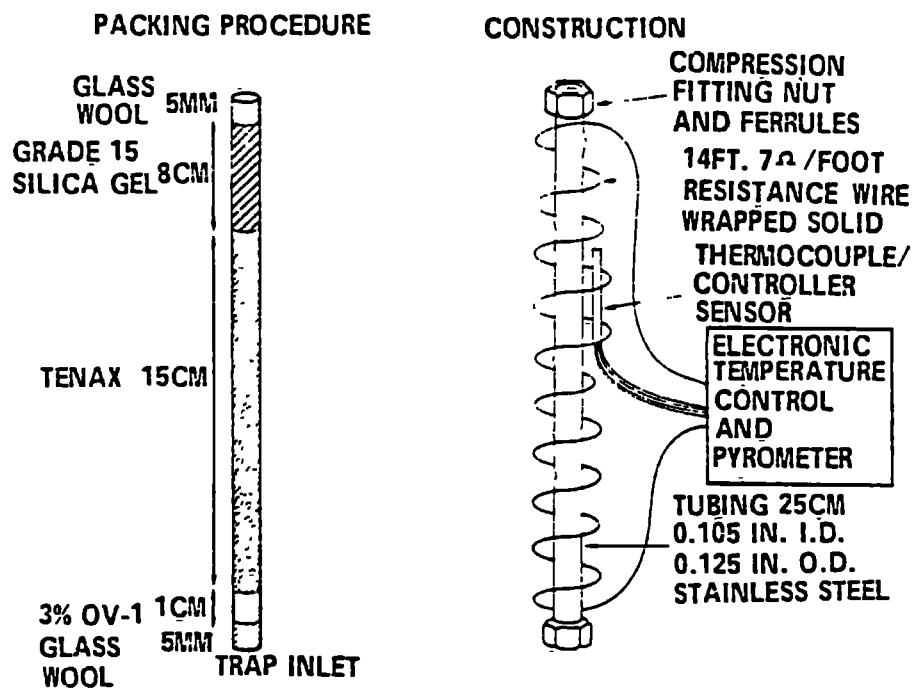


Figure 2. Trap packings and construction to include desorb capability.

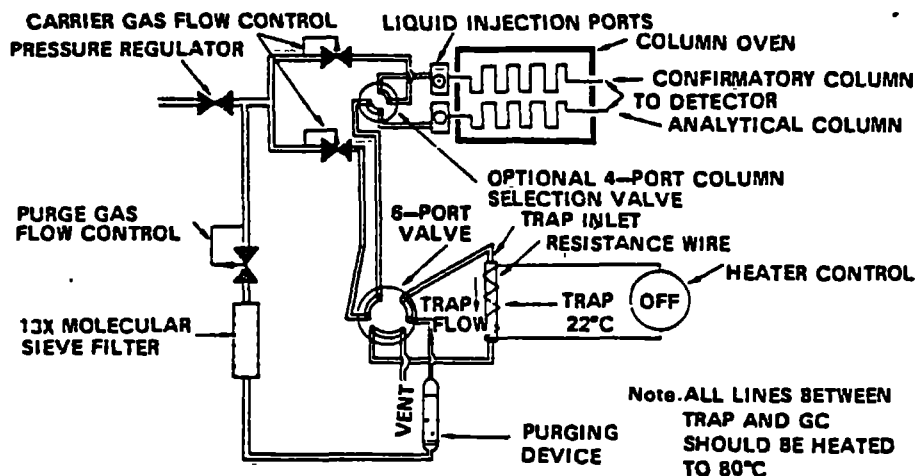


Figure 3. Purge and trap system - purge mode.

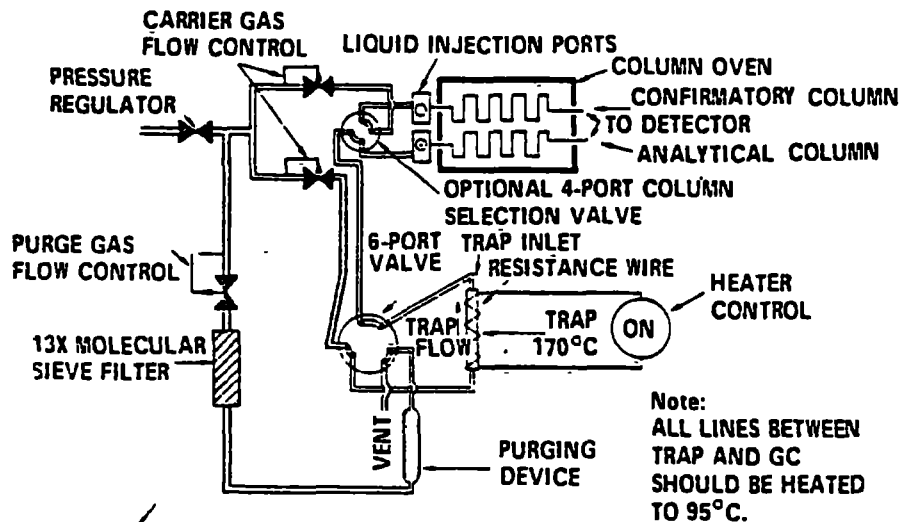


Figure 4. Purge and trap system - desorb mode.

COLUMN: 1% SP-1000 ON CARBOPACK-B
PROGRAM. 45°C FOR 3 MIN, 8°C/MIN TO 220°C
DETECTOR: MASS SPECTROMETER

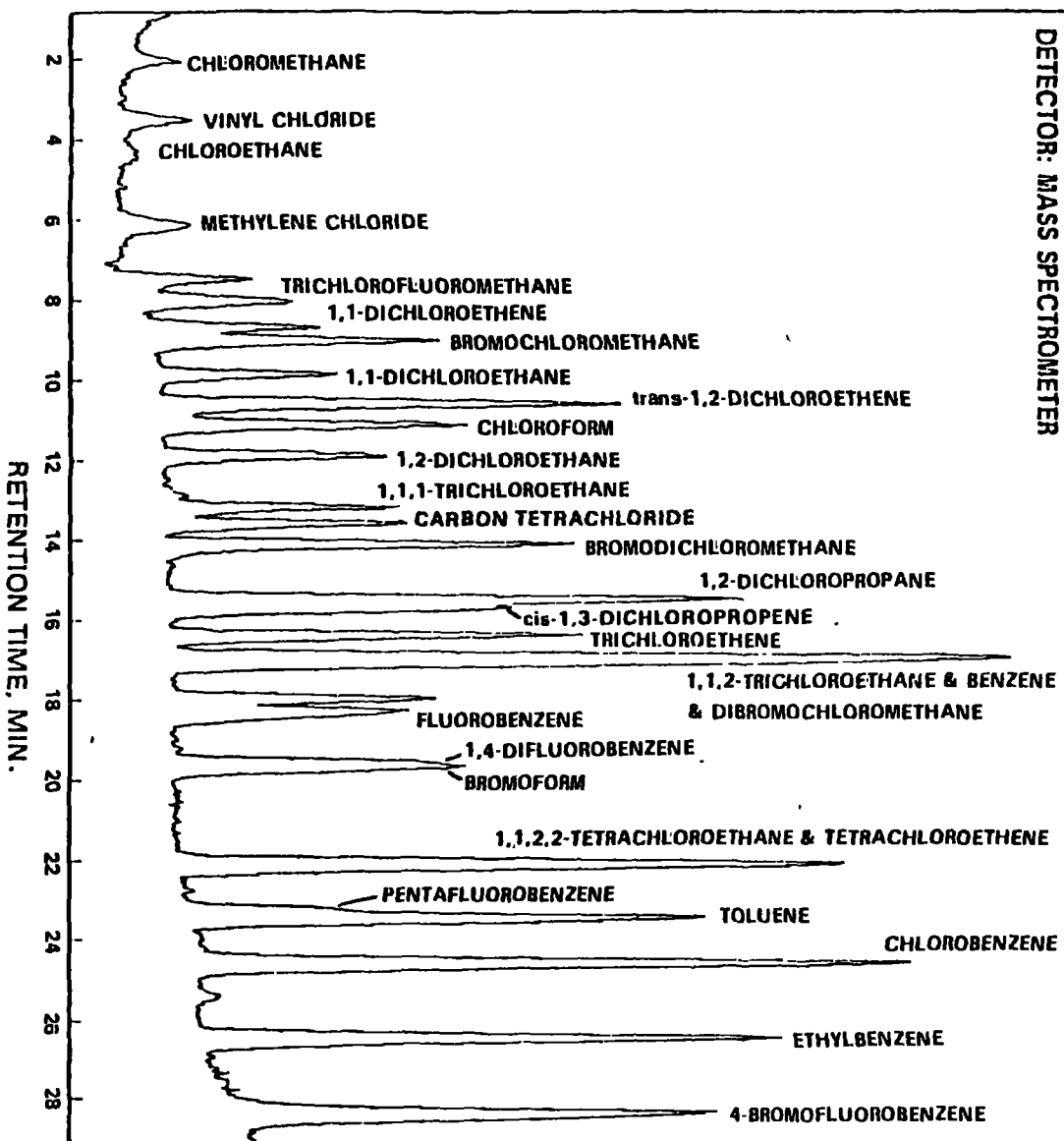


Figure 5. Gas chromatogram of volatile organics.

-708-

Method 625—Base/Neutrals and Acids**1. Scope and Application**

1.1 This method covers the determination of a number of organic compounds that are partitioned into an organic solvent and are amenable to gas chromatography. The parameters listed in Tables 1 and 2 may be qualitatively and quantitatively determined using this method.

1.2 The method may be extended to include the parameters listed in Table 3. Benzidine can be subject to oxidative losses during solvent concentration. Under the alkaline conditions of the extraction step, α -BHC, γ -BHC, endosulfan I and II, and endrin are subject to decomposition. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. The preferred method for each of these parameters is listed in Table 3.

1.3 This is a gas chromatographic/mass spectrometry (GC/MS) method applicable to the determination of the compounds listed in Tables 1, 2, and 3 in municipal and industrial discharges as provided under 40 CFR 136.1.

1.4 The method detection limit (MDL, defined in Section 16.1)¹ for each parameter is listed in Tables 4 and 5. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.5 Any modification to this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5. Depending upon the nature of the modification and the extent of intended use, the applicant may be required to demonstrate that the modifications will produce equivalent results when applied to relevant wastewaters.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph/mass spectrometer and in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately 1-L, is serially extracted with methylene chloride at a pH greater than 11 and again at a pH less than 2 using a separatory funnel or a continuous extractor. The methylene chloride extract is dried, concentrated to a volume of 1 mL, and analyzed by GC/MS. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of three characteristic masses (m/z). Quantitative analysis is performed using either external or internal standard techniques with a single characteristic m/z .

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3.

3.1.1 Glassware must be scrupulously cleaned.² Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 400 °C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Thorough rinsing with such solvents usually eliminates PCB interference. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled.

3.3 The base-neutral extraction may cause significantly reduced recovery of phenol, 2-methylphenol, and 2,4-dimethylphenol. The analyst must recognize that results obtained under these conditions are minimum concentrations.

3.4 The packed gas chromatographic columns recommended for the basic fraction may not exhibit sufficient resolution for certain isomeric pairs including the following: anthracene and phenanthrene; chrysene and benzo(a)anthracene; and benzo(b)fluoranthene and benzo(k)fluoranthene. The gas chromatographic retention time and mass spectra for these pairs of compounds are not sufficiently different to make an unambiguous identification. Alternative techniques should be used to identify and quantify these specific compounds, such as Method 610.

3.5 In samples that contain an inordinate number of interferences, the use of chemical ionization (CI) mass spectrometry may make identification easier. Tables 6 and 7 give characteristic CI ions for most of the compounds covered by this method. The use of CI mass spectrometry to support electron ionization (EI) mass spectrometry is encouraged but not required.

4. Safety.

4.1 The toxicity or carcinogenicity of each reagent used in this method have not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified ** for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, α -BHC, β -BHC, δ -BHC, γ -BHC, dibenzo(a,h)anthracene, N-nitrosodimethylamine, 4,4'-DDT, and polychlorinated biphenyls (PCBs). Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composite sampling

5.1.1 Grab sample bottle—1-L or 1-gal, amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4 °C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used, before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only.):

5.2.1 Separatory funnel—2-L, with Teflon stopcock.

5.2.2 Drying column—Chromatographic column, 19 mm ID, with coarse frit filter disc.

5.2.3 Concentrator tube, Kuderna-Danish—10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.4 Evaporative flask, Kuderna-Danish—500-mL (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.5 Snyder column, Kuderna-Danish—Three all macro (Kontes K-503000-0121 or equivalent).

5.2.6 Snyder column, Kuderna-Danish—Two-ball macro (Kontes K-569001-0219 or equivalent).

5.2.7 Vials—10 to 15-mL, amber glass, with Teflon-lined screw cap.

5.2.8 Continuous liquid—liquid extractor—Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf Extractor, Ace Glass Company, Vineland, N.J., P/N 6841-10 or equivalent.)

5.3 Boiling chips—Approximately 10/40 mesh. Heat to 400 °C for 30 min of Soxhlet extract with methylene chloride.

5.4 Water bath—Heated, with concentric cover, capable of temperature control (±2 °C). The bath should be used in a hood.

5.5 Balance—Analytical, capable of accurately weighing 0.0001 g.

5.6 GC/MS system:

5.6.1 Gas Chromatograph—An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port must be designed for on-column injection when using packed columns and for splitless injection when using capillary columns.

5.6.2 Column for base/neutrals—1.8 m long x 2 mm ID glass, packed with 3% SP-2250 on Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements in Section 16. Guidelines for the use of alternate column packings are provided in Section 13.1.

5.6.3 Column for acids—1.0 m long x 2 mm ID glass, packed with 1% SP-1240DA on Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements in Section 16. Guidelines for the use of alternate column packings are given in Section 13.1.

5.6.4 Mass spectrometer—Capable of scanning from 35 to 450 amu every 7 s or less, utilizing a 70 V (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the criteria in Table 9 when 50 ng of decafluorophenyl phosphine (DFTPP; bis(perfluorophenyl) phenyl phosphine) is injected through the GC inlet.

5.6.5 GC/MS interface—Any GC to MS interface that gives acceptable calibration points at 50 ng per injection for each of the parameters of interest and achieves all acceptable performance criteria (Section 12) may be used. GC to MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

5.6.6 Data system—A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for specific

m/z and plotting such m/z abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.2 Sodium hydroxide solution (10 N)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.3 Sodium thiosulfate—(ACS) Granular.

6.4 Sulfuric acid (1 + 1)—Slowly, add 50 mL of H₂SO₄ (ACS, sp. gr. 1.84) to 50 mL of reagent water.

6.5 Acetone, methanol, methylene chloride—Pesticide quality or equivalent.

6.6 Sodium sulfate—(ACS) Granular, anhydrous. Purify by heating at 400 °C for 4 h in a shallow tray.

6.7 Stock standard solutions (1.00 µg/µL)—standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.7.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

6.7.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4 °C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.7.3 Stock standard solutions must be replaced after six months, or sooner if comparison with quality control check samples indicate a problem.

6.8 Surrogate standard spiking solution—Select a minimum of three surrogate compounds from Table 8. Prepare a surrogate standard spiking solution containing each selected surrogate compound at a concentration of 100 µg/mL in acetone. Addition of 1.00 mL of this solution to 1000 mL of sample is equivalent to a concentration of 100 µg/L of each surrogate standard. Store the spiking solution at 4 °C in Teflon-sealed glass container. The solution should be checked frequently for stability. The solution must be replaced after six months, or sooner if comparison with quality control check standards indicates a problem.

6.9 DFTPP standard—Prepare a 25 µg/mL solution of DFTPP in acetone.

6.10 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Establish gas chromatographic operating parameters equivalent to those indicated in Tables 4 or 5.

7.2 Internal standard calibration procedure—To use this approach, the analyst must select three or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standards is not affected by method or matrix interferences. Some recommended internal standards are listed in Table 8. Use the base peak m/z as the primary m/z for quantification of the standards. If interferences are noted, use one of the next two most intense masses for quantification.

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding appropriate volumes of one or more stock standards to a volumetric flask. To each calibration standard or standard mixture, add a known constant amount of one or more internal standards, and dilute to volume with acetone. One of the calibration standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.2.2 Using injections of 2 to 5 µL, analyze each calibration standard according to Section 13 and tabulate the area of the primary characteristic m/z (Tables 4 and 5) against concentration for each compound and internal standard. Calculate response factors (RF) for each compound using Equation 1.

Equation 1

$$RF = \frac{(A_s)(C_i)}{(A_i)(C_s)}$$

where:

A_s = Area of the characteristic m/z for the parameter to be measured.

A_i = Area of the characteristic m/z for the internal standard.

C_s = Concentration of the internal standard (µg/L).

C_i = Concentration of the parameter to be measured (µg/L).

If the RF value over the working range is a constant (<35% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_i, vs. RF.

7.3 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±20%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control

program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Sections 10.6 and 13.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Before processing any samples, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples is extracted or reagents are changed, a reagent water blank must be processed as a safeguard against laboratory contamination.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 5% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 5% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each parameter of interest at a concentration of 100 µg/mL in acetone. Multiple solutions may be required. PCBs and multicomponent pesticides may be omitted from this test. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards

prepared independently from those used for calibration.

8.2.2 Using a pipet, prepare QC check samples at a concentration of 100 µg/L by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.2.3 Analyze the well-mixed QC check samples according to the method beginning in Section 10 or 11.

8.2.4 Calculate the average recovery (\bar{X}) in µg/L, and the standard deviation of the recovery (s) in µg/L, for each parameter using the four results.

8.2.5 For each parameter compare s and \bar{X} with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6. If s and \bar{X} for all parameters of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual \bar{X} falls outside the range for accuracy, the system performance is unacceptable for that parameter.

Note.—The large number of parameters in Table 6 present a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed.

8.2.6 When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.2.6.1 or 8.2.6.2.

8.2.6.1 Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.2.

8.2.6.2 Beginning with Section 8.2.2, repeat the test only for those parameters that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.2.2.

8.3 The laboratory must, on an ongoing basis, spike at least 5% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing 1 to 20 samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at 100 µg/L or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or 100 µg/L.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as $100(A-B)/T$, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 100 µg/L, the analyst must use either the QC acceptance criteria in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) calculate accuracy (\bar{X}) using the equation in Table 7, substituting the spike concentration (T) for C , (2) calculate overall precision (S) using the equation in Table 7, substituting \bar{X} for \bar{X} , (3) calculate the range for recovery at the spike concentration as $(100 \bar{X}/T) \pm 2.44(100 S'/T)\%$.

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

Note.—The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of single-component parameters in Table 6 must be measured in the sample in Section 8.3, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spike sample.

8.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate (Sections 8.2.1 or 8.3.2) to 1 L of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P) as $100(A/T)\%$, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 6. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the

laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery (\bar{P}) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent interval from $\bar{P}-2s_p$ to $\bar{P}+2s_p$. If $\bar{P}=90\%$ and $s_p=10\%$, for example, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 As a quality control check, the laboratory must spike all samples with the surrogate standard spiking solution as described in Section 10.2, and calculate the percent recovery of each surrogate compound.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be pre-rinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 All sampling must be iced or refrigerated at 4 °C from the time of collection until extraction. Fill the sample bottles and, if residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.⁹ Field test kits are available for this purpose.

9.3 All samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction.

10. Separatory Funnel Extraction

10.1 Samples are usually extracted using separatory funnel techniques. If emulsions will prevent achieving acceptable solvent recovery with separatory funnel extractions, continuous extraction (Section 11) may be used. The separatory funnel extraction scheme described below assumes a sample volume of 1 L. When sample volumes of 2 L are to be extracted, use 250, 100, and 100-mL volumes of methylene chloride for the serial

extraction of the base/neutrals and 200, 100, and 100-mL volumes of methylene chloride for the acids.

10.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel. Pipet 1.00 mL of the surrogate standard spiking solution into the separatory funnel and mix well. Check the pH of the sample with wide-range pH paper and adjust to pH > 11 with sodium hydroxide solution.

10.3 Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask. If the emulsion cannot be broken (recovery of less than 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in Section 11.3.

10.4 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Label the combined extract as the base/neutral fraction.

10.5 Adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Serially extract the acidified aqueous phase three times with 60-mL aliquots of methylene chloride. Collect and combine the extracts in a 250-mL Erlenmeyer flask and label the combined extracts as the acid fraction.

10.6 For each fraction, assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator if the requirements of Section 8.2 are met.

10.7 For each fraction, pour the combined extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.8 Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask for each fraction. Prewet each Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as

required to complete the concentration in 15 to 20 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of methylene chloride. A 5-mL syringe is recommended for this operation.

10.9 Add another one or two clean boiling chips to the concentrator tube for each fraction and attach a two-ball micro-Snyder column. Prewet the Snyder column by adding about 0.5 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches about 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with approximately 0.2 mL of acetone or methylene chloride. Adjust the final volume to 1.0 mL with the solvent. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extracts will be stored longer than two days, they should be transferred to Teflon-sealed screw-cap vials and labeled base/neutral or acid fraction as appropriate.

10.10 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Continuous Extraction

11.1 When experience with a sample from a given source indicates that a serious emulsion problem will result or an emulsion is encountered using a separatory funnel in Section 10.3, a continuous extractor should be used.

11.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Check the pH of the sample with wide-range pH paper and adjust to pH > 11 with sodium hydroxide solution. Transfer the sample to the continuous extractor and using a pipet, add 1.00 mL of surrogate standard spiking solution and mix well. Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 s to rinse the inner surface. Transfer the solvent to the extractor.

11.3 Repeat the sample bottle rinse with an additional 50 to 100-mL portion of methylene chloride and add the rinse to the extractor.

11.4 Add 200 to 500 mL of methylene chloride to the distilling flask, add sufficient reagent water to ensure proper operation, and extract for 24 h. Allow to cool, then detach the distilling flask. Dry, concentrate,

and seal the extract as in Sections 10.6 through 10.9.

11.5 Charge a clean distilling flask with 500 mL of methylene chloride and attach it to the continuous extractor. Carefully, while stirring, adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Extract for 24 h. Dry, concentrate, and seal the extract as in Sections 10.6 through 10.9.

12 Daily GC/MS Performance Tests

12.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria are achieved for DFTPP.¹⁰ Each day that benidine is to be determined, the tailing factor criterion described in Section 12.4 must be achieved. Each day that the acids are to be determined, the tailing factor criterion in Section 12.5 must be achieved.

12.2 These performance tests require the following instrumental parameters:

Electron Energy: 70 V (nominal)
Mass Range: 35 to 450 amu
Scan time: To give at least 5 scans per peak but not to exceed 7 s per scan.

12.3 GC/MS performance test—At the beginning of each day, inject 2 µL (50 ng) of DFTPP standard solution. Obtain a background-corrected mass spectra of DFTPP and confirm that all the key m/z criteria in Table 9 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed. The tailing factor tests in Sections 12.4 and 12.5 may be performed simultaneously with the DFTPP test.

12.4 Column performance test for base/neutrals—At the beginning of each day that the base/neutral fraction is to be analyzed for benidine, the benidine tailing factor must be calculated. Inject 100 ng of benidine either separately or as a part of a standard mixture that may contain DFTPP and calculate the tailing factor. The benidine tailing factor must be less than 3.0. Calculation of the tailing factor is illustrated in Figure 13.¹¹ Replace the column packing if the tailing factor criterion cannot be achieved.

12.5 Column performance test for acids—At the beginning of each day that the acids are to be determined, inject 50 ng of pentachlorophenol either separately or as a part of a standard mix that may contain DFTPP. The tailing factor for pentachlorophenol must be less than 5. Calculation of the tailing factor is illustrated in Figure 13.¹¹ Replace the column packing if the tailing factor criterion cannot be achieved.

13. Gas Chromatography/Mass Spectrometry

13.1 Table 4 summarizes the recommended gas chromatographic operating conditions for the base/neutral fraction. Table 5 summarizes the recommended gas chromatographic operating conditions for the acid fraction. Included in these tables are retention times and MDL that can be achieved under these conditions. Examples of the separations achieved by these columns

are shown in Figures 1 through 12. Other packed or capillary (open-tubular) columns or chromatographic conditions may be used if the requirements of Section 8.2 are met.

13.2 After conducting the GC/MS performance tests in Section 12, calibrate the system daily as described in Section 7.

13.3 If the internal standard calibration procedure is being used, the internal standard must be added to sample extract and mixed thoroughly immediately before injection into the instrument. This procedure minimizes losses due to adsorption, chemical reaction or evaporation.

13.4 Inject 2 to 5 µL of the sample extract or standard into the GC/MS system using the solvent-flush technique.¹² Smaller (1.0 µL) volumes may be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 µL.

13.5 If the response for any m/z exceeds the working range of the GC/MS system, dilute the extract and reanalyze.

13.6 Perform all qualitative and quantitative measurements as described in Sections 14 and 15. When the extracts are not being used for analyses, store them refrigerated at 4°C, protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

14 Qualitative Identification

14.1 Obtain EICPs for the primary m/z and the two other masses listed in Tables 4 and 5. See Section 7.3 for masses to be used with internal and surrogate standards. The following criteria must be met to make a qualitative identification.

14.1.1 The characteristic masses of each parameter of interest must maximize in the same or within one scan of each other.

14.1.2 The retention time must fall within ±30 s of the retention time of the authentic compound.

14.1.3 The relative peak heights of the three characteristic masses in the EICPs must fall within ±20% of the relative intensities of these masses in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library.

14.2 Structural isomers that have very similar mass spectra and less than 30 s difference in retention time, can be explicitly identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

15. Calculations

15.1 When a parameter has been identified, the quantitation of that parameter will be based on the integrated abundance from the EICP of the primary characteristic m/z in Tables 4 and 5. Use the base peak m/z for internal and surrogate standards. If the sample produces an interference for the primary m/z, use a secondary characteristic m/z to quantitate.

Calculate the concentration in the sample using the response factor (RF) determined in Section 7.2.2 and Equation 3.

Equation 3.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(I_i)}{(A_i)(RF)(V_e)}$$

where.

A_s = Area of the characteristic m/z for the parameter or surrogate standard to be measured.

A_i = Area of the characteristic m/z for the internal standard.

I_s = Amount of internal standard added to each extract (µg).

V_e = Volume of water extracted (L).

15.2 Report results in µg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

16. Method Performance

16.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.¹³ The MDL concentrations listed in Tables 4 and 5 were obtained using reagent water.¹⁴ The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

16.2 This method was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5 to 1300 µg/L.¹⁴ Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7.

17. Screening Procedure for 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD)

17.1 If the sample must be screened for the presence of 2,3,7,8-TCDD, it is recommended that the reference material not be handled in the laboratory unless extensive safety precautions are employed. It is sufficient to analyze the base/neutral extract by selected ion monitoring (SIM) GC/MS techniques, as follows:

17.1.1 Concentrate the base/neutral extract to a final volume of 0.2 mL.

17.1.2 Adjust the temperature of the base/neutral column (Section 5.6.2) to 220°C.

17.1.3 Operate the mass spectrometer to acquire data in the SIM mode using the ions at m/z 257, 320 and 322 and a dwell time no greater than 333 milliseconds per mass.

17.1.4 Inject 5 to 7 µL of the base/neutral extract. Collect SIM data for a total of 10 min.

17.1.5 The possible presence of 2,3,7,8-TCDD is indicated if all three masses exhibit simultaneous peaks at any point in the selected ion current profiles.

17.1.6 For each occurrence where the possible presence of 2,3,7,8-TCDD is indicated, calculate and retain the relative abundances of each of the three masses.

17.2 False positives to this test may be caused by the presence of single or coeluting combinations of compounds whose mass spectra contain all of these masses.

17.3 Conclusive results of the presence and concentration level of 2,3,7,8-TCDD can

be obtained only from a properly equipped laboratory through the use of EPA Method 813 or other approved alternate test procedures.

References

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- "Methods 330.4 (Titrimetric, DPD-FAS) and 330.5 (Spectrophotometric, DPD) for Chlorine, Total Residual," Methods for Chemical Analysis of Water and Wastes, EPA-300/4-79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.

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11. McNair, N.M. and Bonelli, E.J. "Basic Chromatography," Consolidated Printing, Berkeley, California, p. 52, 1989.

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TABLE 1—BASE/NEUTRAL EXTRACTABLES

Parameter	STORET No	CAS No.
Acenaphthene	34205	83-32-9
Acenaphthylene	34200	208-96-8
Anthracene	34220	120-12-7
Aldrin	39330	309-00-2
Benzo(a)anthracene	34528	56-55-3
Benzo(b)fluoranthene	34230	205-99-2
Benzo(k)fluoranthene	34242	207-08-9
Benzo(a)pyrene	34247	50-32-8
Benzo(g,h,i)perylene	34521	191-24-2
Benzyl butyl phthalate	34292	85-68-7
β -BHC	39338	319-85-7
δ -BHC	34259	319-86-8
Bis(2-chloroethoxy)ether	34273	111-44-4
Bis(2-chloroethoxy)methane	34278	111-91-1
Bis(2-ethylhexyl)phthalate	39100	117-81-7
Bis(2-chloroisopropyl)ether	34283	108-80-1
4-Bromobenzyl phenyl ether	34636	101-55-3
Chlordane	39350	57-74-9
2-Chloronaphthalene	34581	91-58-7
4-Chlorophenyl phenyl ether	34641	7005-72-3
Chrysene	34320	218-01-9
4,4'-DDD	39310	72-54-8
4,4'-DDE	39320	72-55-9
4,4'-DDT	39300	50-29-3
D-benzol(a,h)anthracene	34556	53-70-3
D-n-butylphthalate	39110	84-74-2
1,3-Dichlorobenzene	34566	541-73-1
1,2-Dichlorobenzene	34536	95-50-1
1,4-Dichlorobenzene	34571	106-46-7
3,3'-Dichlorobenzidine	34631	91-84-1
Dieldrin	39380	60-57-1
D-ethyl phthalate	34336	84-68-2
Dimethyl phthalate	34341	131-11-3
2,4-Dinitrotoluene	34611	121-14-2
2,6-Dinitrotoluene	34626	608-20-2
D-n-octylphthalate	34596	117-84-0
Endosulfan sulfate	34351	1031-07-8

TABLE 1.—BASE/NEUTRAL EXTRACTABLES—Continued

Parameter	STORET No	CAS No
Endrin aldehyde	34368	7421-93-4
Fluorene	34378	208-44-0
Fluorene	34381	86-73-7
Heptachlor	39410	76-44-8
Heptachlor epoxide	39420	1024-57-3
Hexachlorobenzene	39700	118-74-1
Hexachlorobutadiene	34391	87-89-3
Hexachlorocyclopentadiene	34386	87-72-1
Indeno(1,2,3-cd)pyrene	34403	193-39-5
Isophorone	34408	78-59-1
Naphthalene	34698	91-20-3
Nitrobenzene	34447	98-95-3
N-Nitrosodimethylamine	34428	621-84-7
PCB-1016	34671	12674-11-2
PCB-1221	39488	11104-28-2
PCB-1232	39492	11741-18-5
PCB-1242	39496	53469-21-9
PCB-1248	39500	12672-29-6
PCB-1254	39504	11997-89-1
PCB-1260	39508	11096-82-5
Phenanthrene	34481	85-01-8
Pyrene	34469	129-00-0
Toxachene	39400	8001-33-2
1,2,4-Trichlorobenzene	34551	120-82-1

TABLE 2.—ACID EXTRACTABLES

Parameter	STORET No	CAS No
4-Chloro-3-methylphenol	34452	59-50-7
2-Chlorophenol	34586	95-57-8
2,4-Dichlorophenol	34601	123-83-2
2,4-Dimethylphenol	34606	105-67-9
2,4-Dinitrophenol	34618	51-28-5
2-Methyl-4,6-dinitrophenol	34657	534-52-1
2-Nitrophenol	34531	55-75-5
4-Nitrophenol	34648	100-02-7
Pentachlorophenol	35232	87-86-5
Phenol	34694	103-95-2
2,4,6-Trichlorophenol	34521	88-05-2

TABLE 3.—ADDITIONAL EXTRACTABLE PARAMETERS*

Parameter	STORET No.	CAS No	Method
Benzidine	39120	92-87-5	605
β -BHC	39337	319-84-6	608
δ -BHC	39340	58-69-8	608
Endosulfan I	34361	959-58-8	608
Endosulfan II	34356	33213-65-9	608
Endrin	39390	72-20-8	608
Hexachlorocyclopentadiene	34396	77-47-4	812
N-Nitrosodimethylamine	34438	62-75-9	807
N-Nitrosophenylamine	34433	88-30-6	607

* See Section 1.2.

TABLE 4.—CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC MASSES FOR BASE/NEUTRAL EXTRACTABLES

Parameter	Retention time (min)	Method detection limit ($\mu\text{g/L}$)	Characteristic masses					
			Electron impact			Chemical ionization		
			Primary	Secondary	Secondary	Methane	Methane	Methane
1,3-Dichlorobenzene	7.4	1.9	146	148	113	146	148	150
1,4-Dichlorobenzene	7.8	4.4	146	148	113	146	148	150
Hexachlorobenzene	8.4	1.6	117	201	199	199	201	203
Bis(2-chloroethyl) ether	8.4	5.7	93	93	95	93	107	109
1,2-Dichlorobenzene	8.4	1.9	146	148	113	146	148	150
Bis(2-chloroisopropyl) ether	9.3	5.7	45	77	79	77	135	137
N-Nitrosodimethylamine			130	42	101			
Nitrobenzene	11.1	1.9	77	123	85	124	152	164
Hexachlorobutadiene	11.4	0.9	225	223	227	223	225	227
1,2,4-Trichlorobenzene	11.8	1.9	180	182	145	181	183	200
Isophorone	11.9	2.2	82	95	138	138	167	178
Naphthalene	12.1	1.6	128	129	127	129	157	169
Bis(2-chloroethoxy) methane	12.2	5.3	93	95	123	95	137	137
Hexachlorocyclopentadiene*	13.9		237	235	272	235	237	236
2-Chloronaphthalene	15.9	1.9	172	164	127	163	151	203
Acenaphthylene	17.4	3.5	152	151	153	152	153	161

TABLE 4.—CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC MASSES FOR BASE/NEUTRAL EXTRACTABLES—Continued

Parameter	Retention time (min)	Method detection limit (µg/L)	Characteristic masses					
			Electron impact			Chemical ionization		
			Primary	Secondary	Secondary	Methane	Methane	Methane
Acenaphthene	17.8	1.9	154	153	152	154	155	183
Dimethyl phthalate	18.3	1.6	163	194	164	151	163	164
2,6-Dinitrotoluene	18.7	1.9	165	89	121	183	211	223
Fluorene	19.5	1.9	166	165	167	166	167	195
4-Chlorophenyl phenyl ether	19.5	4.2	204	208	141			
2,4-Dinitrotoluene	19.8	5.7	165	63	182	183	211	223
Dimethylphthalate	20.1	1.9	149	177	150	177	223	251
N-Nitrosodiphenylamine*	20.5	1.9	169	168	167	189	170	198
Hexachlorobenzene	21.0	1.9	264	142	249	284	256	289
β-BHC*	21.1		183	191	109			
4-Bromophenyl phenyl ether	21.2	1.9	248	250	141	249	251	277
δ-BHC*	22.4		183	181	109			
Phenanthrene	22.8	5.4	179	179	178	178	179	207
Anthracene	22.8	1.9	178	179	176	178	179	207
β-BHC	23.4	4.2	181	183	109			
Heptachlor	23.4	1.9	100	272	274			
δ-BHC	23.7	3.1	183	109	181			
Aldrin	24.0	1.8	66	263	220			
Diethyl phthalate	24.7	2.5	149	150	104	149	205	279
Heptachlor epoxide	25.6	2.2	353	355	351			
Endosulfan I*	26.4		237	338	341			
Fluoranthene	26.5	2.2	202	101	100	203	231	243
Dieldrin	27.2	2.5	79	263	279			
4,4'-DDE	27.2	5.6	246	248	176			
Pyrene	27.3	1.9	202	101	100	203	231	243
Endrin*	27.9		81	263	82			
Endosulfan II*	28.6		237	339	341			
4,4'-DDD	28.6	2.8	235	237	165			
Benzo(a)pyrene	28.8	4.4	184	92	185	185	213	225
4,4'-DDT	29.3	4.7	235	237	165			
Endosulfan sulfate	29.8	5.6	272	387	422			
Endrin aldehyde			67	345	250			
Butyl benzyl phthalate	29.9	2.5	149	91	208	149	299	327
Bis(2-ethylhexyl) phthalate	30.6	2.5	149	187	279	149		
Chrysene	31.5	2.5	228	226	229	228	229	257
Benzo(a)anthracene	31.5	7.8	229	229	229	228	229	237
3,3'-Dichlorobenzidine	32.2	16.5	252	254	126			
Di-n-octyl phthalate	32.5	2.5	149					
Benzo(b)fluoranthene	34.8	4.8	252	253	125	252	253	281
Benzo(k)fluoranthene	34.9	2.5	252	253	125	252	253	281
Benzo(a)pyrene	36.4	2.5	252	253	125	252	253	281
Indeno(1,2,3-c) dipyrene	42.7	3.7	276	138	277	275	277	305
Dioxanthrene/anthracene	43.2	2.5	278	139	279	278	279	307
Benzo(g)hperylene	45.1	4.1	275	138	277	276	277	305
N-Nitrosodiphenylamine*			42	74	44			
Chlordane*	18-30		373	375	377			
Toxaphene*	25-34		159	231	233			
PCB 1016*	18-30		224	260	294			
PCB 1221*	15-30	30	190	224	260			
PCB 1232*	15-32		190	224	280			
PCB 1242*	15-32		224	260	294			
PCB 1248*	12-34		294	330	352			
PCB 1254*	22-34	36	294	330	352			
PCB 1260*	23-32		330	362	394			

* See Section 1.2

* These compounds are mixtures of various isomers (See figures 2 thru 12)

Column conditions: Supelcoport (100/120 mesh) coated with 3% SP-2250 packed in a 1.3 m long x 2mm ID glass column with helium carrier gas at 30 mL/min flow rate. Column temperature held isothermal at 50 °C for 4 min, then programmed at 8 °C/min to 270 °C and held for 30 min.

TABLE 5.—CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC MASSES FOR ACID EXTRACTABLES

Parameter	Retention time (min)	Method detection limit (µg/L)	Characteristic masses					
			Electron impact			Chemical ionization		
			Primary	Secondary	Secondary	Methane	Methane	Methane
2-Chlorophenol	5.8	3.3	128	64	130	129	131	157
2-Nitrophenol	6.5	3.6	139	65	103	140	168	122
Phenol	8.0	1.5	94	85	68	95	123	135
2,4-Dimethylphenol	9.4	2.7	122	107	121	123	151	163
2,4-Dichlorophenol	9.8	2.7	162	164	98	163	165	167
2,4,6-Trichlorophenol	11.8	2.7	196	198	200	197	199	201
4-Chloro-3-methylphenol	13.2	3.0	142	107	144	143	171	183
2,4-Dinitrophenol	15.9	4.2	184	83	154	195	213	225
2-Methyl-4,6-dinitrophenol	16.2	2.4	198	182	77	199	227	239
Pentachlorophenol	17.5	3.6	266	264	268	267	265	269
4-Nitrophenol	20.3	2.4	65	139	109	140	168	122

Column conditions: Supelcoport (100/120 mesh) coated with 1% SP-1240DA packed in a 1.8 m long x 2mm ID glass column with helium carrier gas at 30 mL/min flow rate. Column temperature held isothermal at 70 °C for 2 min then programmed at 8 °C/min to 200 °C.

TABLE 6.—QC ACCEPTANCE CRITERIA—METHOD 625

Parameter	Test conclusion ($\mu\text{g/L}$)	Limits for s ($\mu\text{g/L}$)	Range for X ($\mu\text{g/L}$)	Range for P, P _s (Percent)
Acenaphthene	100	27.8	80.1-122.3	47-145
Acenaphthylene	100	40.2	53.5-126.0	33-145
Adren	100	39.0	7.2-152.2	D-168
Anthracene	100	32.0	43.4-118.0	27-133
Benzo(a)anthracene	100	27.6	41.8-133.0	33-143
Benzo(b)fluoranthene	100	38.8	42.0-140.4	24-158
Benzo(k)fluoranthene	100	32.3	25.2-145.7	11-182
Benzo(a)pyrene	100	39.0	31.7-148.0	17-163
Benzo(g,h,i)perylene	100	58.9	D-195.0	D-219
Benzo(butyl) phthalate	100	23.4	D-139.9	D-152
B-EH ₂	100	31.5	41.5-130.6	24-149
B-EH ₃	100	21.6	D-100.0	C-110
Bis(2-chloroethyl)ether	100	55.0	42.9-126.0	12-158
Bis(2-chloroethoxy)methane	100	34.5	49.2-164.7	33-184
Bis(2-chloroisopropyl)ether	100	46.3	62.9-138.6	38-166
Bis(2-methylphenyl)phthalate	100	41.1	26.9-136.8	8-158
4-Bromophenyl phenyl ether	100	23.0	64.9-114.4	53-127
2-Chloronaphthalene	100	13.0	64.5-113.5	60-118
4-Chlorophenyl phenyl ether	100	33.4	38.4-144.7	25-158
Chrysene	100	48.3	44.1-139.9	17-168
4,4'-DCE	100	31.0	D-134.5	D-145
4,4'-DDE	100	32.0	19.2-119.7	4-136
4,4'-DDT	100	61.6	D-170.6	D-203
Dibenz(a,h)anthracene	100	70.0	D-198.7	D-227
D-n-butyl phthalate	100	16.7	8.4-111.0	1-118
1,2-Dichlorobenzene	100	30.9	48.6-112.0	32-129
1,3-Dichlorobenzene	100	41.7	16.7-153.9	D-172
1,4-Dichlorobenzene	100	32.1	37.3-105.7	20-124
3,3'-Dichlorobenzidine	100	71.4	8.2-212.5	D-262
Dieldrin	100	30.7	44.3-119.3	29-138
Dibutyl phthalate	100	26.5	D-100.0	D-114
D-methyl phthalate	100	23.2	D-100.0	D-112
2,4-Dinitro toluene	100	21.8	47.5-126.9	39-139
2,6-Dinitrotoluene	100	29.6	68.1-136.7	50-158
D-n-octyl phthalate	100	31.4	18.6-131.8	4-148
Erdosutan sulfate	100	16.7	D-103.5	D-107
Erdos aldehyde	100	32.5	D-188.8	D-209
Fluoranthene	100	32.8	42.9-121.3	26-137
Fluorene	100	20.7	71.6-108.4	59-121
Heptachlor	100	37.2	D-172.2	D-182
Heptachlor epoxide	100	54.7	70.9-109.4	25-155
Hexachlorobenzene	100	24.9	7.8-141.5	C-152
Hexachlorobutadiene	100	26.3	37.8-102.2	21-118
Hexachlorocyclopentadiene	100	24.5	55.2-100.0	40-113
Indeno(1,2,3-cd)pyrene	100	44.6	D-150.9	D-171
Iscophorone	100	63.3	46.6-160.2	21-196
Naphthalene	100	30.1	35.8-119.6	21-133
Nitrobenzene	100	39.3	54.3-157.6	35-180
N-Nitrosod-n-propylamine	100	55.4	13.6-197.9	D-230
PCB-1260	100	54.2	19.3-121.0	D-164
Phenanthrene	100	20.6	65.2-106.7	54-120
Pyrene	100	25.2	69.6-100.0	52-115
1,2,4-Trichlorobenzene	100	28.1	57.3-129.2	44-142
4-Chloro-3-methylphenol	100	37.2	40.6-121.9	22-147
2-Chlorophenol	100	28.7	36.2-120.4	23-134
2,4-Dichlorophenol	100	25.4	52.5-121.7	39-135
2,4-Dichloromethanol	100	25.1	41.8-109.0	32-119
2,3-Dichlorophenol	100	49.8	D-172.9	D-191
2-Methyl-4,5-dinitrophenol	100	95.2	53.0-100.0	D-181
2-Nitrophenol	100	35.2	45.0-165.7	29-182
4-Nitrophenol	100	47.2	13.0-106.5	D-132
Pentachlorophenol	100	48.9	58.1-151.9	14-176
Phenol	100	22.6	16.6-100.0	5-112
2,4,5-Trichlorophenol	100	31.7	52.4-129.2	37-144

s = Standard deviation for four recovery measurements, in $\mu\text{g/L}$ (Section 8.2.4)X = Average recovery for four recovery measurements, in $\mu\text{g/L}$ (Section 8.2.4)P, P_s = Percent recovery measured (Section 8.3.2, Section 8.4.2)

D = Detected, result must be greater than zero.

Note: These criteria are based directly upon the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7.

TABLE 7. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 625

Parameter	Accuracy, as recovery, X' ($\mu\text{g/L}$)	Single analyst precision, S _x ($\mu\text{g/L}$)	Overall precision, S' ($\mu\text{g/L}$)
Acenaphthene	0.98C+0.19	0.15X-0.12	0.21X-0.67
Acenaphthylene	0.89C+0.74	0.24X-1.08	0.26X-0.54
Adren	0.78C+1.88	0.27X-1.28	0.43X-1.13
Anthracene	0.80C-0.68	0.21X-0.32	0.27X-0.54
Benzo(a)anthracene	0.88C-0.60	0.15X+0.93	0.26X-0.28
Benzo(b)fluoranthene	0.83C-1.80	0.22X+0.43	0.29X-0.96
Benzo(k)fluoranthene	0.87C-1.56	0.19X-1.03	0.25X-0.40
Benzo(a)pyrene	0.90C-0.13	0.22X+0.48	0.32X-1.35
Benzo(g,h,i)perylene	0.98C-0.86	0.29X+2.40	0.51X-0.44
Benzo(butyl) phthalate	0.68C-1.68	0.18X+0.94	0.53X-0.92
B-EH ₂	0.87C-0.84	0.20X-0.58	0.30X-1.94
B-EH ₃	0.29C-1.09	0.34X+0.66	0.93X-0.17
Bis(2-chloroethyl)ether	0.86C-1.54	0.35X-0.98	0.35X+0.10

TABLE 7 METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 625—Continued

Parameter	Accuracy, as recovery, \bar{X} ($\mu\text{g/L}$)	Single analyst precision S_x ($\mu\text{g/L}$)	Overall precision, S' ($\mu\text{g/L}$)
Bis(2-chloroethoxy)methane	112C-5.04	0.16 \bar{X} +1.34	0.25 \bar{X} -2.01
Bis(2-chloroisopropyl)ether	103C-2.31	0.24 \bar{X} +0.28	0.25 \bar{X} -1.04
Bis(2-ethylhexyl)phthalate	0.84C-1.18	0.26 \bar{X} +0.73	0.26 \bar{X} -0.87
4-Bromophenyl phenyl ether	0.91C-1.34	0.13 \bar{X} +0.66	0.16 \bar{X} -0.68
2-Chloronaphthalene	0.89C+0.01	0.07 \bar{X} +0.52	0.13 \bar{X} -0.34
4-Chlorophenyl phenyl ether	0.91C+0.53	0.20 \bar{X} -0.94	0.30 \bar{X} -0.48
Chrysene	0.93C-1.00	0.28 \bar{X} -0.13	0.33 \bar{X} -0.09
4,4-DDD	0.56C-0.40	0.29 \bar{X} -0.32	0.66 \bar{X} -0.98
4,4-DDE	0.70C-0.54	0.26 \bar{X} -1.17	0.39 \bar{X} -1.04
4,4-DDT	0.79C-3.28	0.42 \bar{X} -0.19	0.55 \bar{X} -0.58
Dibenz(a,h)anthracene	0.88C+4.72	0.30 \bar{X} -8.51	0.59 \bar{X} -0.25
Di-n-butyl phthalate	0.59C+0.71	0.13 \bar{X} +1.16	0.39 \bar{X} -0.60
1,2-Dichlorobenzene	0.80C-0.28	0.20 \bar{X} +0.47	0.24 \bar{X} -0.39
1,3-Dichlorobenzene	0.06C-0.70	0.25 \bar{X} +0.68	0.41 \bar{X} -0.11
1,4-Dichlorobenzene	0.73C-1.47	0.24 \bar{X} -0.23	0.29 \bar{X} -0.36
3,3'-Dichlorobenzidine	1.23C-12.85	0.28 \bar{X} +7.33	0.47 \bar{X} -3.45
Dieldrin	0.82C-0.18	0.20 \bar{X} -0.18	0.28 \bar{X} -0.07
Diethyl phthalate	0.43C+1.00	0.28 \bar{X} +1.44	0.52 \bar{X} +0.22
Dimethyl phthalate	0.20C+1.03	0.54 \bar{X} +0.19	1.05 \bar{X} -0.92
2,4-Dinitrotoluene	0.92C-4.81	0.12 \bar{X} +1.06	0.21 \bar{X} +1.50
2,6-Dinitrotoluene	1.06C-3.60	0.14 \bar{X} +1.28	0.19 \bar{X} -0.35
Di-n-octylphthalate	0.78C-0.79	0.21 \bar{X} +1.19	0.37 \bar{X} -1.19
Endosulfan sulfate	0.39C+0.41	0.12 \bar{X} +2.47	0.63 \bar{X} -1.03
Endrin aldehyde	0.76C-3.86	0.18 \bar{X} -3.91	0.73 \bar{X} -0.62
Fluoranthene	0.81C+1.10	0.22 \bar{X} -0.73	0.28 \bar{X} -0.60
Fluorene	0.90C-0.00	0.12 \bar{X} +0.28	0.13 \bar{X} -0.91
Heptachlor	0.87C-2.97	0.24 \bar{X} -0.56	0.50 \bar{X} -0.23
Heptachlor epoxide	0.92C-1.67	0.33 \bar{X} -0.48	0.28 \bar{X} -0.64
Hexachlorobenzene	0.74C+0.66	0.18 \bar{X} -0.10	0.43 \bar{X} -0.52
Hexachlorobutadiene	0.71C-1.01	0.19 \bar{X} +0.92	0.28 \bar{X} -0.49
Hexachlorocyclopentadiene	0.73C-0.83	0.17 \bar{X} -0.67	0.17 \bar{X} -0.80
Indeno(1,2,3-cd)pyrene	0.78C-3.10	0.29 \bar{X} +1.48	0.50 \bar{X} -0.44
Isophorone	1.12C+1.41	0.27 \bar{X} +0.77	0.33 \bar{X} -0.26
Naphthalene	0.78C-1.58	0.21 \bar{X} -0.41	0.30 \bar{X} -0.88
Nitrobenzene	1.09C-3.05	0.19 \bar{X} -0.92	0.27 \bar{X} -0.21
N-Nitrosodi-n-propylamine	1.12C-6.22	0.27 \bar{X} -0.68	0.44 \bar{X} -0.47
PCB-1260	0.81C-10.86	0.35 \bar{X} -3.61	0.43 \bar{X} -1.82
Phenanthrene	0.97C-0.06	0.12 \bar{X} +0.57	0.15 \bar{X} +0.25
Pyrene	0.84C-0.16	0.18 \bar{X} -0.06	0.15 \bar{X} -0.31
1,2,4-Trichlorobenzene	0.94C-0.79	0.15 \bar{X} +0.85	0.21 \bar{X} -0.39
4-Chloro-3-methylphenol	0.84C+0.35	0.23 \bar{X} -0.75	0.29 \bar{X} -1.31
2-Chlorophenol	0.78C+0.29	0.18 \bar{X} -1.46	0.26 \bar{X} -0.97
2,4-Dichlorophenol	0.87C+0.13	0.15 \bar{X} -1.25	0.21 \bar{X} -1.28
2,4-Dimethylphenol	0.71C+4.41	0.18 \bar{X} +1.21	0.22 \bar{X} -1.31
2,4-Dinitrophenol	0.81C-18.04	0.38 \bar{X} -2.36	0.42 \bar{X} -26.29
2-Methyl-4,6-dinitrophenol	1.04C-28.04	0.10 \bar{X} +42.29	0.26 \bar{X} -23.10
2-Nitrophenol	1.07C-1.15	0.16 \bar{X} +1.94	0.27 \bar{X} -2.60
4-Nitrophenol	0.61C-1.22	0.38 \bar{X} -2.57	0.44 \bar{X} -3.24
Pentachlorophenol	0.93C-1.99	0.24 \bar{X} +3.03	0.30 \bar{X} -4.33
Phenol	0.43C-1.28	0.28 \bar{X} -0.73	0.35 \bar{X} -0.58
2,3,6-Trichlorophenol	0.91C-0.18	0.16 \bar{X} -2.22	0.22 \bar{X} -1.81

\bar{X} = Expected recovery for one or more measurements of a sample containing a concentration of C, in $\mu\text{g/L}$
 s_x = Expected single analyst standard deviation of measurements at an average concentration found of \bar{X} in $\mu\text{g/L}$
 S' = Expected interlaboratory standard deviation of measurements at an average concentration found of \bar{X} in $\mu\text{g/L}$
C = True value for the concentration in $\mu\text{g/L}$
 \bar{X} = Average recovery found for measurements of samples containing a concentration of C, in $\mu\text{g/L}$

TABLE 8—SUGGESTED INTERNAL AND SURROGATE STANDARDS

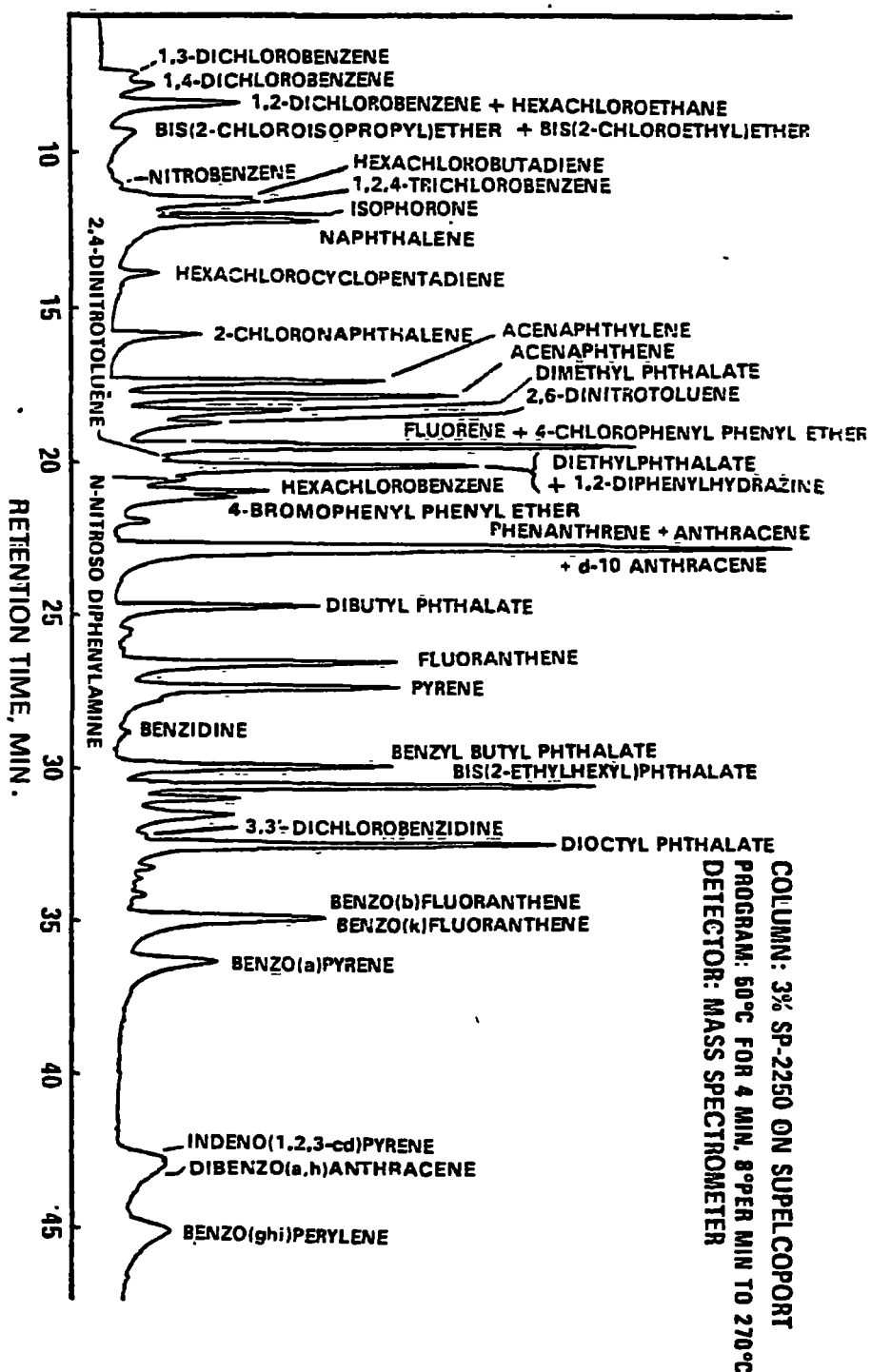
Base/neutral fraction	Acid fraction
Aniline- d_6	2-Fluorophenol
Anthracene- d_{10}	Pentafluorophenol
Benzo(a)anthracene- d_{12}	Phenol- d_6
4,4'-Dibromodiphenyl	2-Pentafluoromethyl phenol
4,4'-Dibromodiphenyl	
Dibromodiphenyl	
Decafluorobiphenyl	
2,2,1-Difluorobiphenyl	
4-Fluorophenyl	
1-Fluorophenyl	
2-Fluorophenyl	
Naphthalene- d_8	
Nitrobenzene- d_5	
2,3,4,5,6-Pentafluorobiphenyl	
Phenanthrene- d_{12}	
Pyrene- d_{10}	

TABLE 9.—DFTPP KEY MASSES AND ABUNDANCE CRITERIA

Mass	m/z Abundance criteria
51	30-80 percent of mass 198.
69	Less than 2 percent of mass 69
70	Less than 2 percent of mass 69
127	40-60 percent of mass 198.
197	Less than 1 percent of mass 198
198	Base peak, 100 percent relative abundance
199	5-9 percent of mass 198
275	10-30 percent of mass 198
365	Greater than 1 percent of mass 198
441	Present but less than mass 443
442	Greater than 40 percent of mass 198
443	17-23 percent of mass 442

BILLING CODE 6560-60-M

Figure 1. Gas chromatogram of base/neutral fraction.



-59-

COLUMN: 1% SP-1240DA ON SUPELCOPORT
PROGRAM: 70°C FOR 2 MIN, 8°C/MIN TO 200°C
DETECTOR: MASS SPECTROMETER.

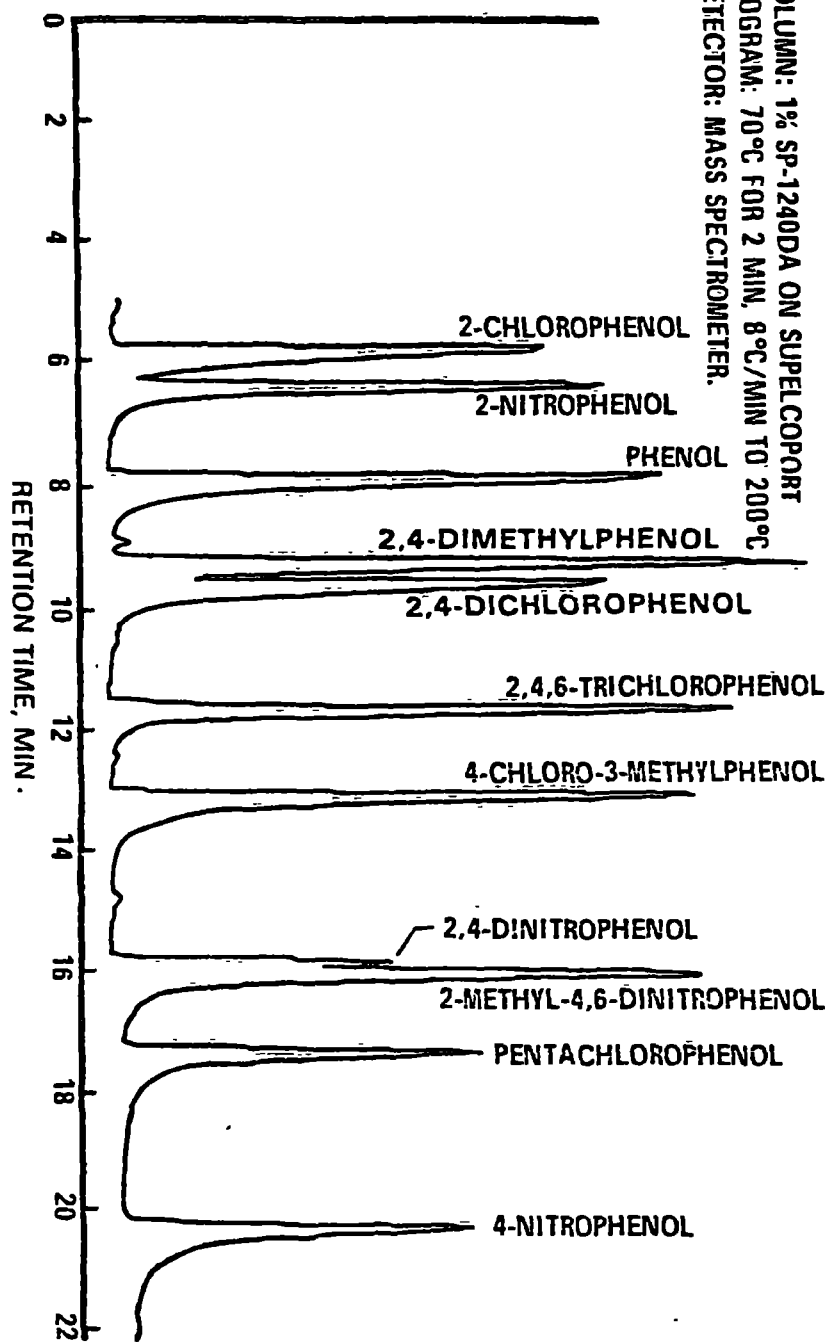


Figure 2. Gas chromatogram of acid fraction.

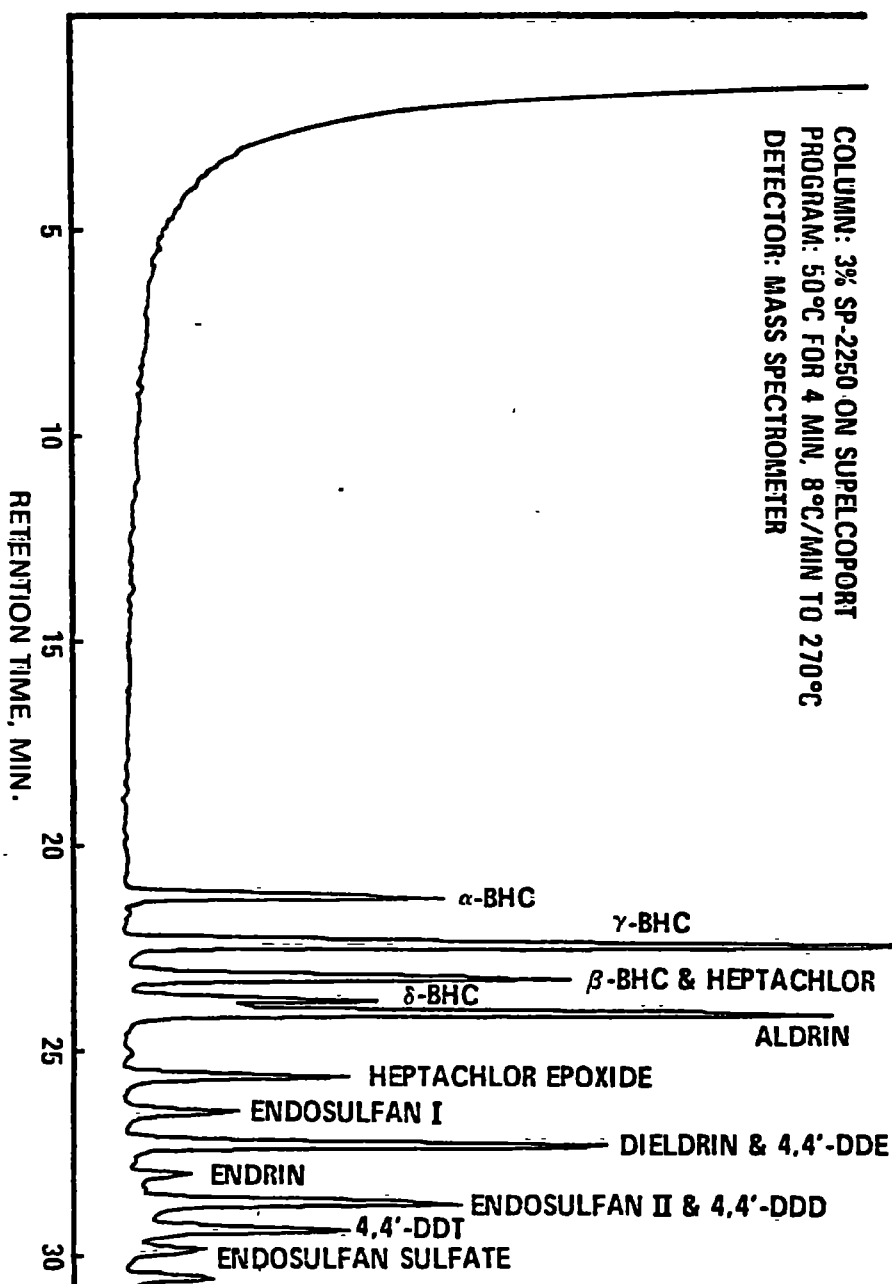


Figure 3. Gas chromatogram of pesticide fraction.

-766-

COLUMN: 3% SP-2150 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN, 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

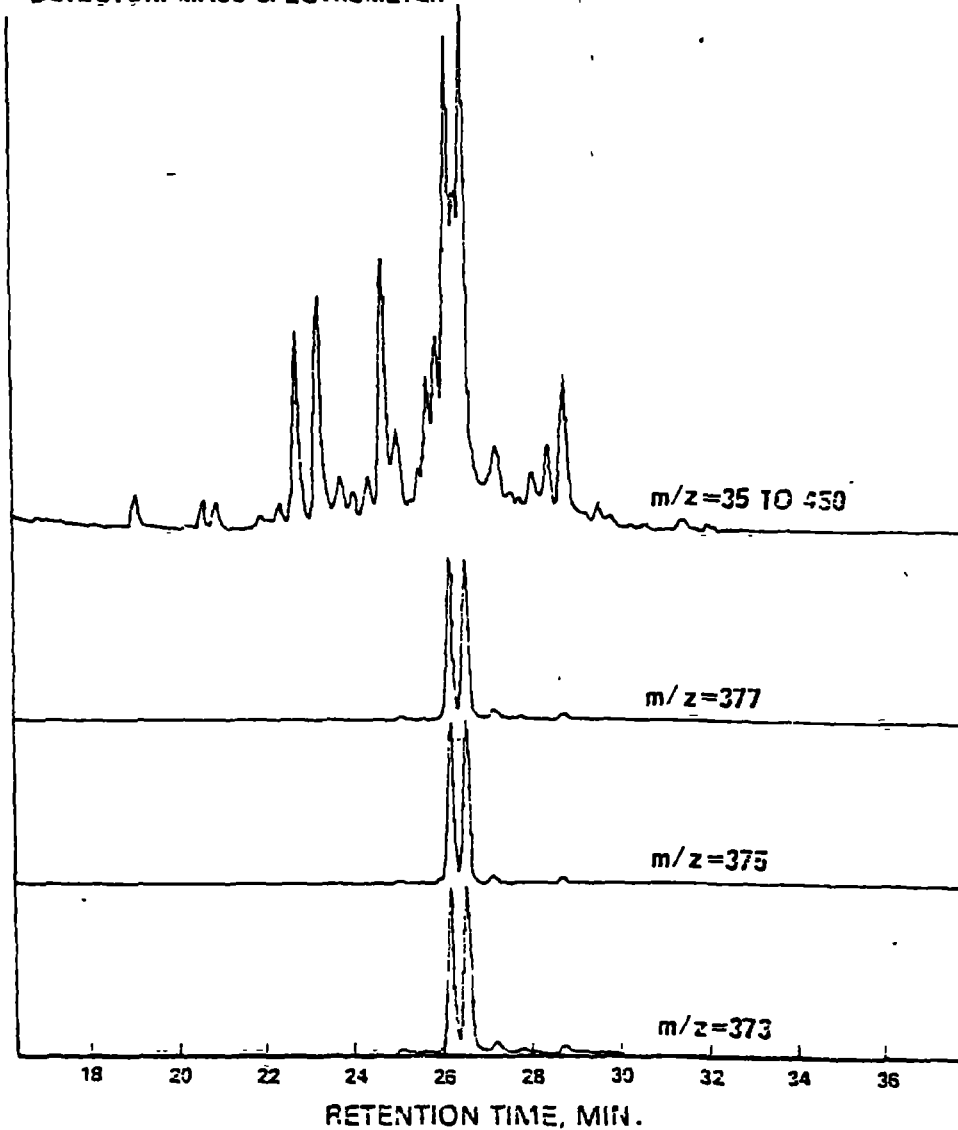


Figure 4. Gas chromatogram of chlordane.

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN, 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

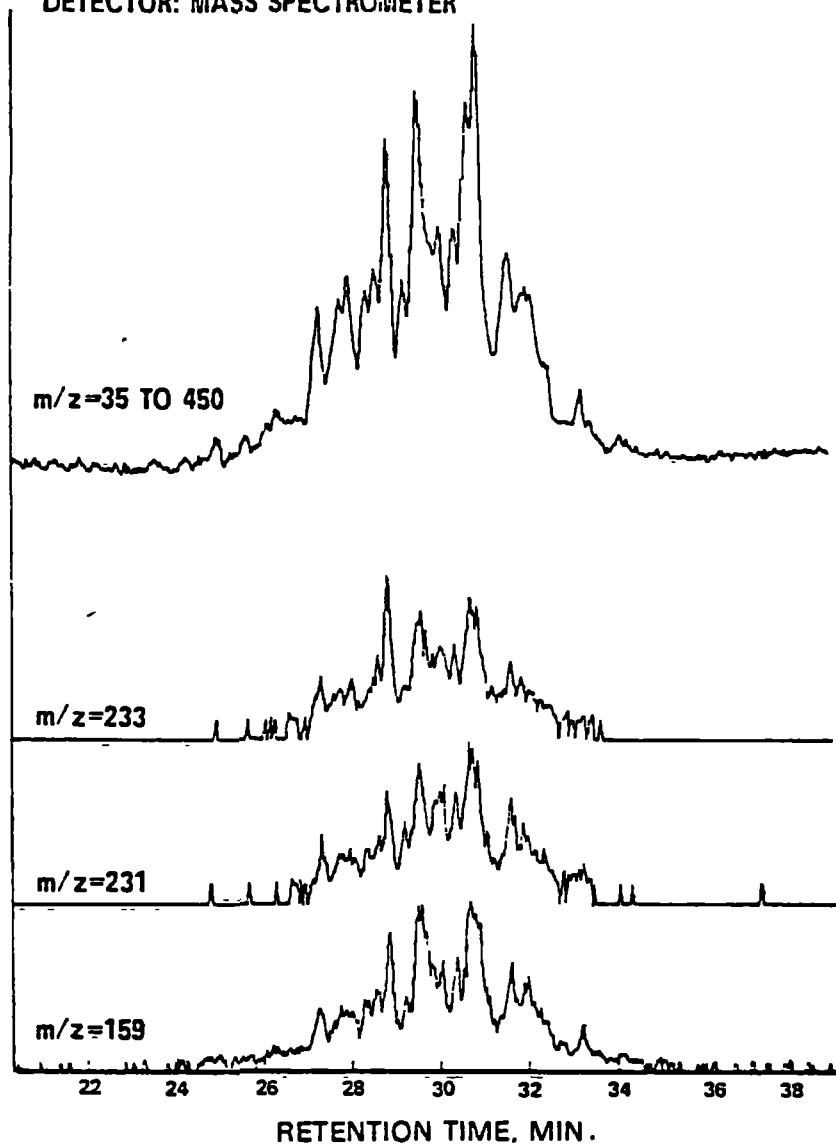


Figure 5. Gas chromatogram of toxaphene.

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN, 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

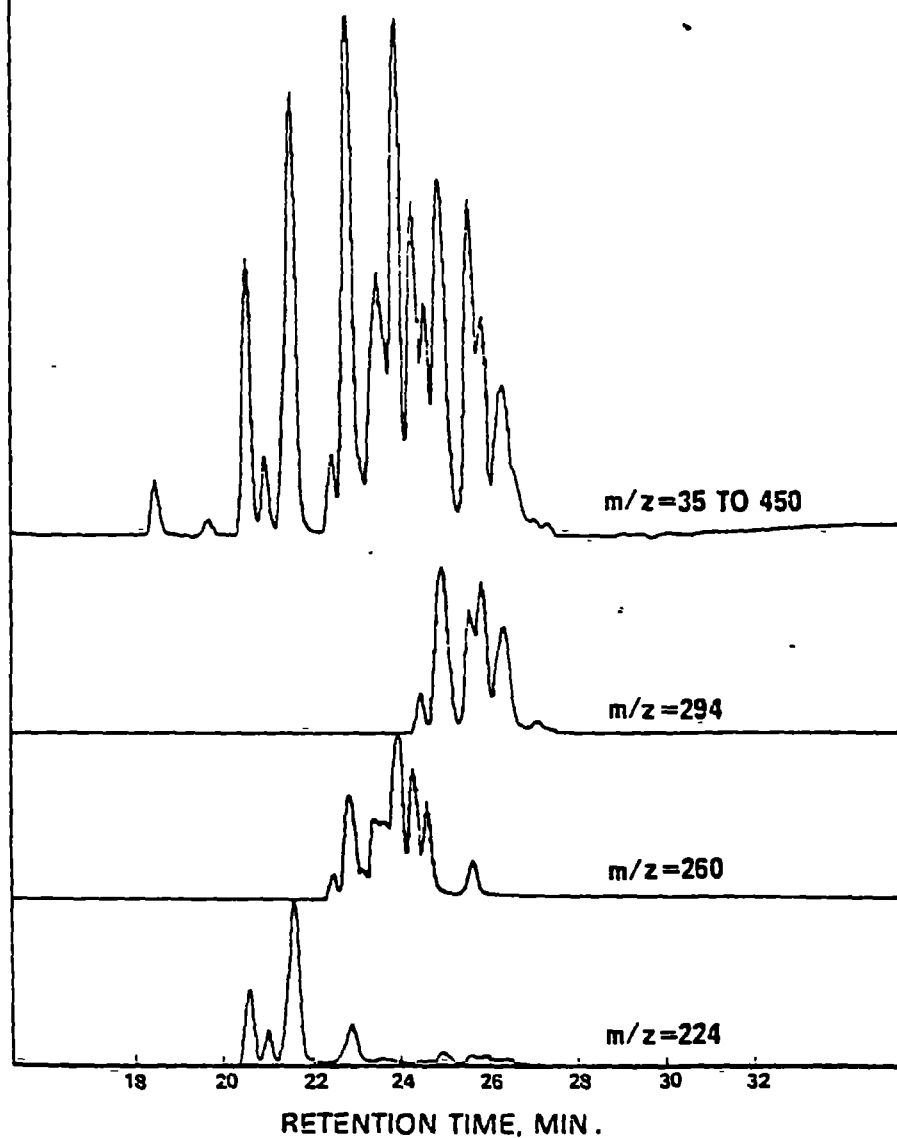


Figure 6. Gas chromatogram of PCB-1016.

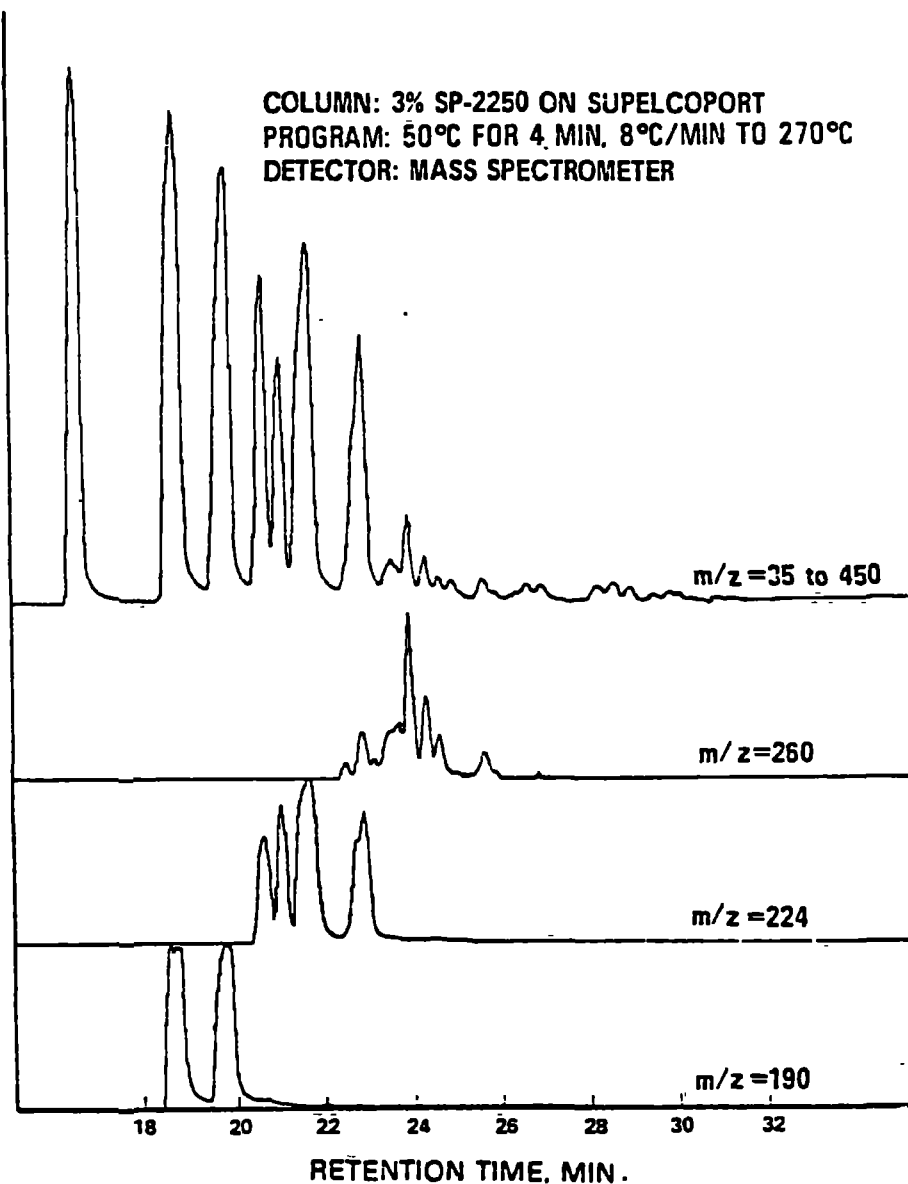


Figure 7. Gas chromatogram of PCB-1221.

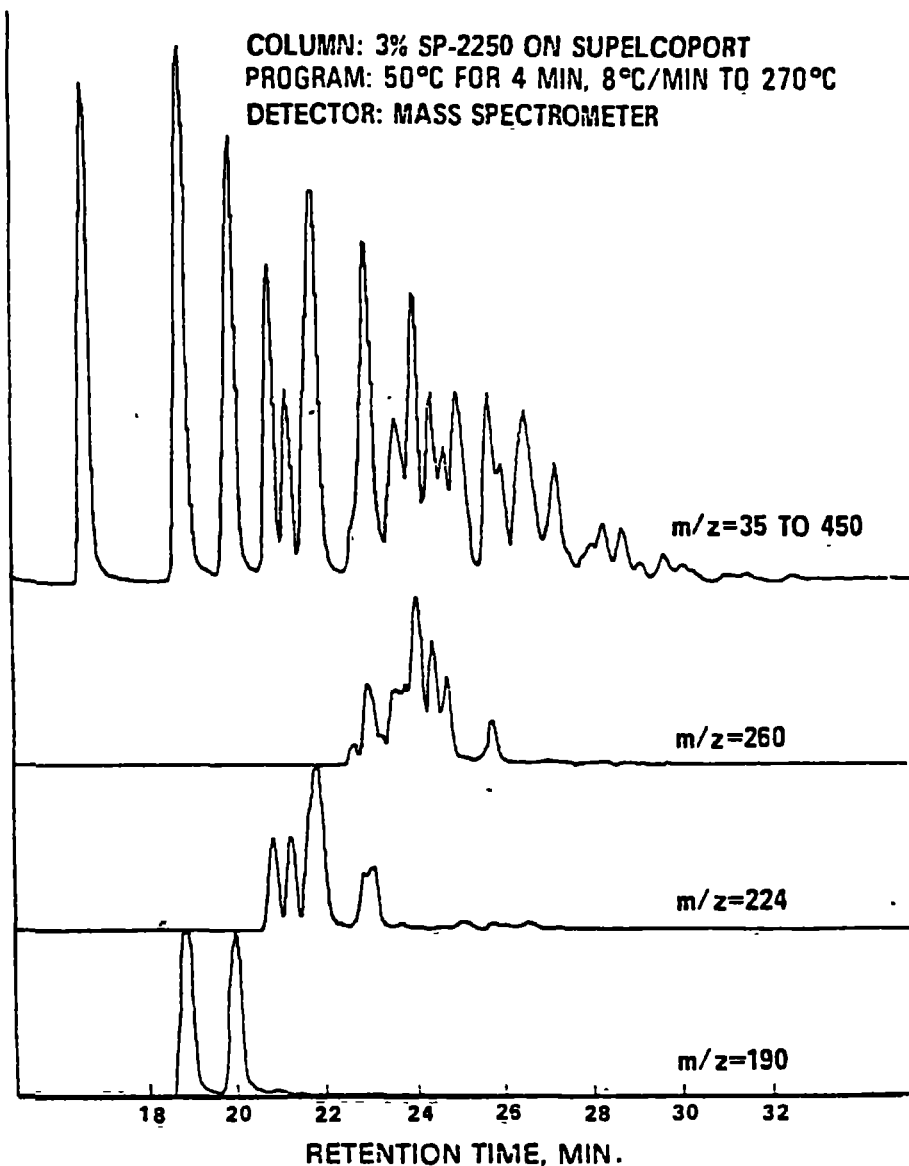


Figure 8. Gas chromatogram of PCB-1232.

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN, 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

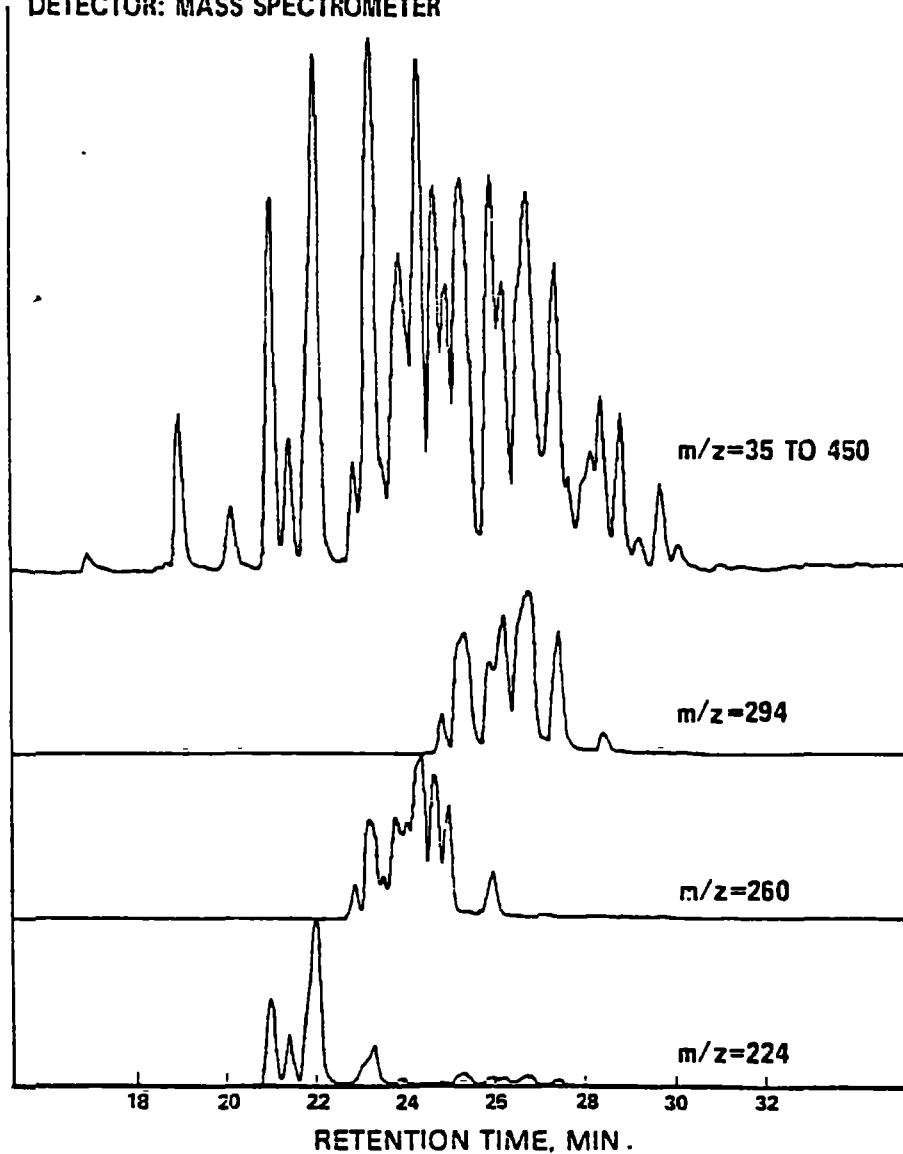


Figure 9. Gas chromatogram of PCB-1242.

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN, 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

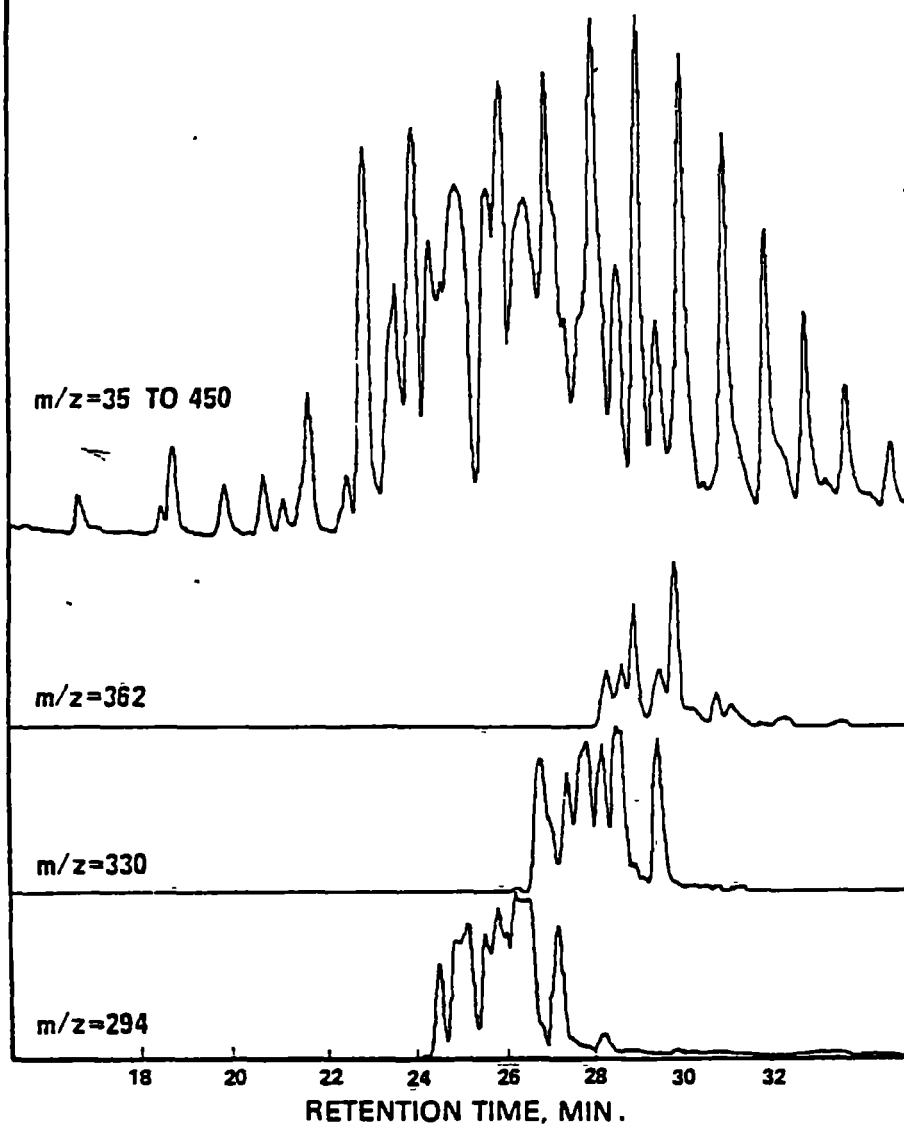


Figure 10. Gas chromatogram of PCB-1248.

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN, 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

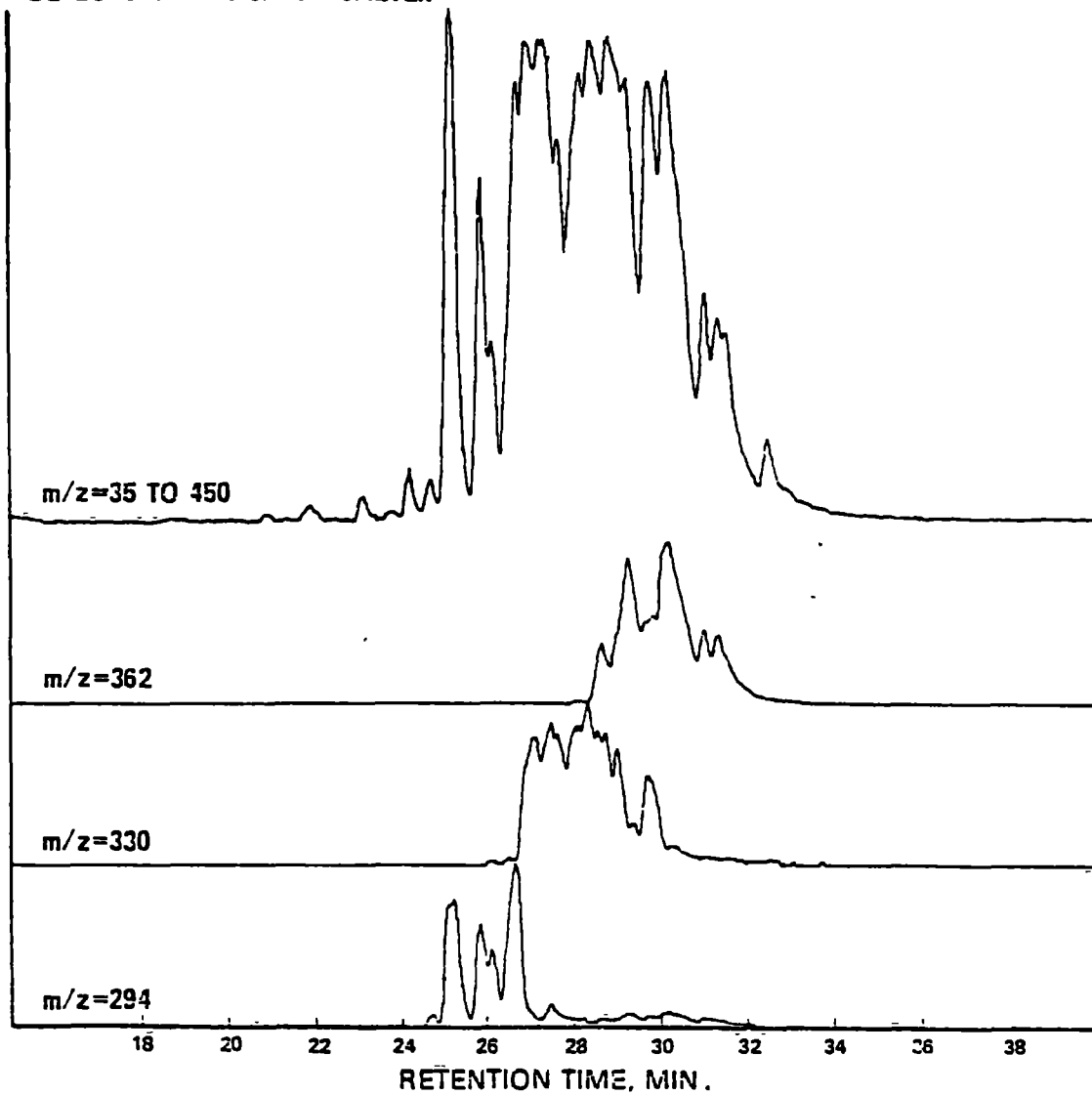


Figure 11. Gas chromatogram of PCB-1254.

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN, 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

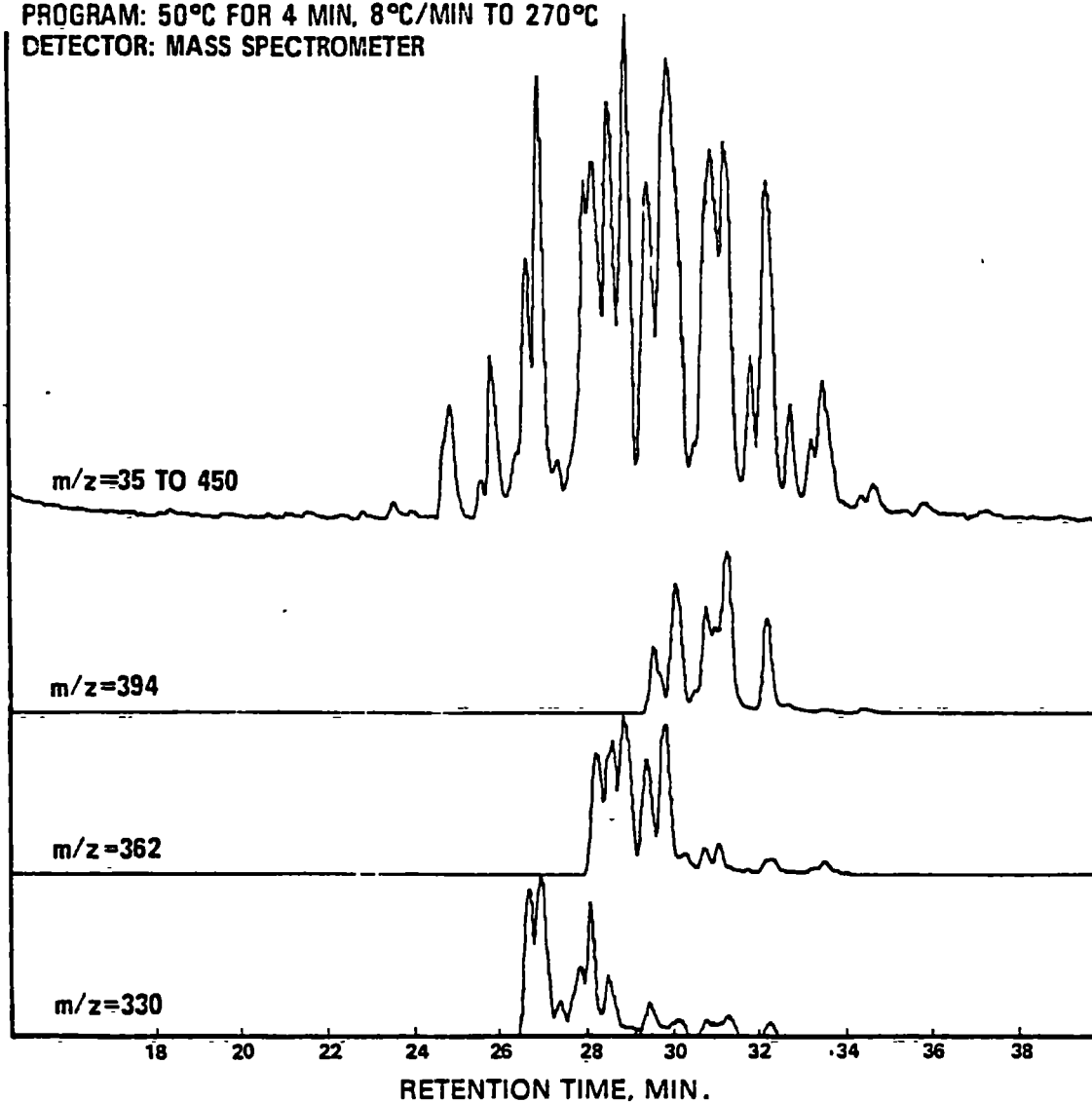
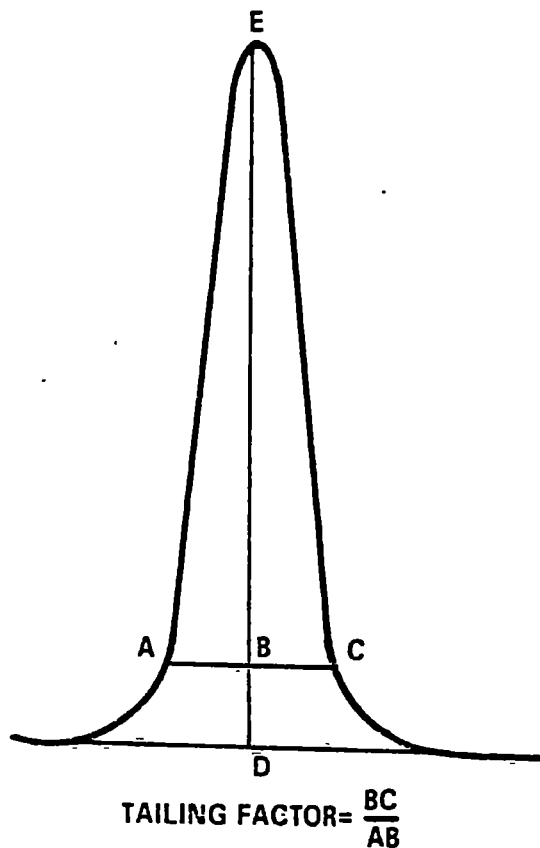


Figure 12. Gas chromatogram of PCB-1260.



Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Tailing Factor = $\frac{12}{11} \approx 1.1$

Figure 13. Tailing factor calculation.



Test Method

Inductively Coupled Plasma— Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes—Method 200.7

1. Scope and Application

1.1 This method may be used for the determination of dissolved, suspended, or total elements in drinking water, surface water, domestic and industrial wastewaters.

1.2 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interference are taken into account. This is especially true when dissolved solids exceed 1500 mg/L (See 5).

1.3 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps *must* be taken to correct for potential interference effects (See 5).

1.4 Table 1 lists elements for which this method applies along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detection limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be

added as more information becomes available and as required.

1.5 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instructions provided by the manufacturer of the particular instrument.

2. Summary of Method

2.1 The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the

determination of trace elements Background must be measured adjacent to analyte lines on samples during analysis The position selected for the background intensity measurement on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result The possibility of additional interferences named in 5.1 (and tests for their presence as described in 5.2) should also be recognized and appropriate corrections made

3. Definitions

3.1 Dissolved — Those elements which will pass through a 0.45 μm membrane filter

3.2 Suspended — Those elements which are retained by a 0.45 μm membrane filter

3.3 Total — The concentration determined on an unfiltered sample following vigorous digestion (9.3), or the sum of the dissolved plus suspended concentrations (9.1 plus 9.2)

3.4 Total recoverable — The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid (9.4)

3.5 Instrumental detection limit — The concentration equivalent to a signal, due to the analyte which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength

3.6 Sensitivity — The slope of the analytical curve, i.e. functional relationship between emission intensity and concentration

3.7 Instrument check standard — A multielement standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis (See 7.6.1)

3.8 Interference check sample — A solution containing both interfering and analyte elements of known concentration that can be used to

verify background and interelement correction factors (See 7.6.2)

3.9 Quality control sample — A solution obtained from an outside source having known, concentration values to be used to verify the calibration standards (See 7.6.3)

3.10 Calibration standards — A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve) (See 7.4)

3.11 Linear dynamic range — The concentration range over which the analytical curve remains linear

3.12 Reagent blank — A volume of deionized, distilled water containing the same acid matrix as the calibration standards carried through the entire analytical scheme (See 7.5.2)

3.13 Calibration blank — A volume of deionized, distilled water acidified with HNO_3 and HCl (See 7.5.1)

3.14 Method of standard addition — The standard addition technique involves the use of the unknown and the unknown plus a known amount of standard (See 10.6.1)

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (14.7, 14.8 and 14.9) for the information of the analyst

5. Interferences

5.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

5.1.1 Spectral interferences can be categorized as 1) overlap of a spectral line from another element, 2)

unresolved overlap of molecular band spectra, 3) background contribution from continuous or recombination phenomena, and 4) background contribution from stray light from the line emission of high concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data requiring the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multielement instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array. Listed in Table 2 are some interference effects for the recommended wavelengths given in Table 1. The data in Table 2 are intended for use only as a rudimentary guide for the indication of potential spectral interferences. For this purpose, linear relations between concentration and intensity for the analytes and the interferences can be assumed.

The interference information which was collected at the Ames Laboratory is expressed at analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interferent element. The suggested use of this information is as follows: Assume that arsenic (at 193.696 nm) is to be determined in a sample containing approximately 10 mg/L of aluminum. According to Table 2, 100 mg/L of aluminum would yield a false signal for arsenic equivalent to approximately 1.3 mg/L . Therefore, 10 mg/L of aluminum would result in a false signal for arsenic equivalent to approximately 0.13 mg/L . The reader is cautioned that other analytical systems may exhibit somewhat different levels of interference than those shown in Table 2, and that the interference effects must be evaluated for each individual system.

Only those interferences listed were investigated and the blank spaces in Table 2 indicate that measurable interferences were not observed for the interferent concentrations listed in Table 3. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2-5% of the peaks generated by the

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analyte concentrations also listed in Table 3

At present information on the listed silver and potassium wavelengths are not available but it has been reported that second order energy from the magnesium 383.231 nm wavelength interferes with the listed potassium line at 766.491 nm

5.1.2 Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or acid concentrations. The use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they must be reduced by dilution of the sample and/or utilization of standard addition techniques. Another problem which can occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aerosol flow-rate causing instrumental drift. Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution have been used to control this problem. Also, it has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

5.1.3 Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not pronounced with the ICP technique, however, if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.

5.2 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in 5.2.1 through 5.2.4, will ensure the analyst that neither positive nor negative interference effects are operative on any of the analyte elements thereby distorting the accuracy of the reported values.

5.2.1 Serial dilution—If the analyte concentration is sufficiently high (min-

imally a factor of 10 above the instrumental detection limit after dilution), an analysis of a dilution should agree within 5 % of the original determination (or within some acceptable control limit (14.3) that has been established for that matrix). If not, a chemical or physical interference effect should be suspected.

5.2.2 Spike addition—The recovery of a spike addition added at a minimum level of 10X the instrumental detection limit (maximum 100X) to the original determination should be recovered to within 90 to 110 percent or within the established control limit for that matrix. If not, a matrix effect should be suspected. The use of a standard addition analysis procedure can usually compensate for this effect. *Caution*: The standard addition technique does not detect coincident spectral overlap. If suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended. (See 5.2.3)

5.2.3 Comparison with alternate method of analysis—When investigating a new sample matrix, comparison tests may be performed with other analytical techniques such as atomic absorption spectrometry, or other approved methodology.

5.2.4 Wavelength scanning of analyte line region—If the appropriate equipment is available, wavelength scanning can be performed to detect potential spectral interferences.

6. Apparatus

6.1 Inductively Coupled Plasma-Atomic Emission Spectrometer

6.1.1 Computer controlled atomic emission spectrometer with background correction

6.1.2 Radiofrequency generator

6.1.3 Argon gas supply, welding grade or better

6.2 Operating conditions — Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument. It is the

responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain quality control data confirming instrument performance and analytical results.

7. Reagents and standards

7.1 Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.

7.1.1 Acetic acid, conc. (sp. gr. 1.06)

7.1.2 Hydrochloric acid, conc. (sp. gr. 1.19)

7.1.3 Hydrochloric acid (1-1). Add 500 mL conc. HCl (sp. gr. 1.19) to 400 mL deionized, distilled water and dilute to 1 liter.

7.1.4 Nitric acid, conc. (sp. gr. 1.41)

7.1.5 Nitric acid (1-1). Add 500 mL conc. HNO₃ (sp. gr. 1.41) to 400 mL deionized, distilled water and dilute to 1 liter.

7.2 Deionized, distilled water. Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized distilled water for the preparation of all reagents, calibration standards and as dilution water. The purity of this water must be equivalent to ASTM Type II reagent water of Specification D 1193 (14.6).

7.3 Standard stock solutions may be purchased or prepared from ultra high purity grade chemicals or metals. All salts must be dried for 1 h at 105°C unless otherwise specified. (CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.) Typical stock solution preparation procedures follow.

7.3.1 Aluminum solution, stock. 1 mL = 100 µg Al. Dissolve 0.100 g of aluminum metal in an acid mixture of 4 mL of (1-1) HCl and 1 mL of conc. HNO₃ in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a 1-liter flask, add an additional 10 mL of (1-1) HCl and dilute to 1,000 mL with deionized distilled water.

7.3.2 Antimony solution, stock. 1 mL = 100 µg Sb. Dissolve 0.2669 g K(SbO)₃·C₄H₄O₆ in deionized distilled water, add 10 mL (1-1) HCl and dilute to 1,000 mL with deionized, distilled water.

7 3 3 Arsenic solution stock 1 mL = 100 µg As Dissolve 0.1320 g of As_2O_3 in 100 mL of deionized distilled water containing 0.4 g NaOH. Acidify the solution with 2 mL conc HNO_3 and dilute to 1 000 mL with deionized distilled water.

7 3 4 Barium solution stock 1 mL = 100 µg Ba Dissolve 0.1516 g BaCl_2 (dried at 250 °C for 2 hrs) in 10 mL deionized distilled water with 1 mL (1-1) HCl. Add 10.0 mL (1-1) HCl and dilute to 1 000 mL with deionized distilled water.

7 3 5 Beryllium solution stock 1 mL = 100 µg Be Do not dry Dissolve 1.966 g $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ in deionized distilled water add 10.0 mL conc HNO_3 and dilute to 1 000 mL with deionized distilled water.

7 3 6 Boron solution stock 1 mL = 100 µg B Do not dry Dissolve 0.5716 g anhydrous H_3BO_3 in deionized distilled water dilute to 1 000 mL. Use a reagent meeting ACS specifications, keep the bottle tightly stoppered and store in a desiccator to prevent the entrance of atmospheric moisture.

7 3 7 Cadmium solution stock 1 mL = 100 µg Cd Dissolve 0.1142 g CdO in a minimum amount of (1-1) HNO_3 . Heat to increase rate of dissolution. Add 10.0 mL conc HNO_3 and dilute to 1 000 mL with deionized distilled water.

7 3 8 Calcium solution stock 1 mL = 100 µg Ca Suspend 0.2498 g CaCO_3 dried at 180 °C for 1 h before weighing in deionized distilled water and dissolve cautiously with a minimum amount of (1-1) HNO_3 . Add 10.0 mL conc HNO_3 and dilute to 1 000 mL with deionized distilled water.

7 3 9 Chromium solution stock 1 mL = 100 µg Cr Dissolve 0.1923 g of CrO_3 in deionized distilled water. When solution is complete acidify with 10 mL conc HNO_3 and dilute to 1 000 mL with deionized distilled water.

7 3 10 Cobalt solution stock 1 mL = 100 µg Co Dissolve 0.1000 g of cobalt metal in a minimum amount of (1-1) HNO_3 . Add 10.0 mL (1-1) HCl and dilute to 1 000 mL with deionized distilled water.

7 3 11 Copper solution stock 1 mL = 100 µg Cu Dissolve 0.1252 g CuO in a minimum amount of (1-1) HNO_3 . Add 10.0 mL conc HNO_3 and dilute to 1 000 mL with deionized distilled water.

7 3 12 Iron solution stock 1 mL = 100 µg Fe Dissolve 0.1430 g Fe_2O_3 in a warm mixture of 20 mL (1-1) HCl and 2 mL of conc HNO_3 . Cool add an additional 5 mL of conc HNO_3 and dilute to 1 000 mL with deionized distilled water.

7 3 13 Lead solution stock 1 mL = 100 µg Pb Dissolve 0.1599 g $\text{Pb}(\text{NO}_3)_2$ in minimum amount of (1-1) HNO_3 . Add 10.0 mL conc HNO_3 and dilute to 1 000 mL with deionized distilled water.

7 3 14 Magnesium solution stock 1 mL = 100 µg Mg Dissolve 0.1658 g MgO in a minimum amount of (1-1) HNO_3 . Add 10.0 mL conc HNO_3 and dilute to 1 000 mL with deionized distilled water.

7 3 15 Manganese solution stock 1 mL = 100 µg Mn Dissolve 0.1000 g of manganese metal in the acid mixture 10 mL conc HCl and 1 mL conc HNO_3 and dilute to 1 000 mL with deionized distilled water.

7 3 16 Molybdenum solution stock 1 mL = 100 µg Mo Dissolve 0.2043 g $(\text{NH}_4)_2\text{MoO}_4$ in deionized distilled water and dilute to 1 000 mL.

7 3 17 Nickel solution stock 1 mL = 100 µg Ni Dissolve 0.1000 g of nickel metal in 10 mL hot conc HNO_3 cool and dilute to 1 000 mL with deionized distilled water.

7 3 18 Potassium solution stock 1 mL = 100 µg K Dissolve 0.1907 g KCl dried at 110 °C, in deionized distilled water dilute to 1 000 mL.

7 3 19 Selenium solution stock 1 mL = 100 µg Se Do not dry Dissolve 0.1727 g H_2SeO_3 (actual assay 94.6%) in deionized distilled water and dilute to 1 000 mL.

7 3 20 Silica solution stock 1 mL = 100 µg SiO_2 Do not dry Dissolve 0.4730 g $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ in deionized distilled water. Add 10.0 mL conc HNO_3 and dilute to 1 000 mL with deionized distilled water.

7 3 21 Silver solution stock 1 mL = 100 µg Ag Dissolve 0.1575 g AgNO_3 in 100 mL of deionized distilled water and 10 mL conc HNO_3 . Dilute to 1 000 mL with deionized distilled water.

7 3 22 Sodium solution stock 1 mL = 100 µg Na Dissolve 0.2542 g NaCl in deionized distilled water. Add 10.0 mL conc HNO_3 and dilute to 1 000 mL with deionized distilled water.

7 3 23 Thallium solution stock 1 mL = 100 µg Tl Dissolve 0.1303 g TlNO_3 in deionized distilled water. Add 10.0 mL conc HNO_3 and dilute to 1 000 mL with deionized distilled water.

7 3 24 Vanadium solution stock 1 mL = 100 µg V Dissolve 0.2297 NH_4VO_3 in a minimum amount of conc HNO_3 . Heat to increase rate of dissolution. Add 10.0 mL conc HNO_3 and dilute to 1 000 mL with deionized distilled water.

7 3 25 Zinc solution stock 1 mL = 100 µg Zn Dissolve 0.1245 g ZnO in a minimum amount of dilute HNO_3 . Add 10.0 mL conc HNO_3 and dilute to 1 000 mL with deionized distilled water.

7 4 Mixed calibration standard solutions—Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (See 7 4 1 thru 7 4 5). Add 2 mL of (1-1) HCl and dilute to 100 mL with deionized distilled water (See Notes 1 and 6). Prior to preparing the mixed standards each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to a FEP fluorocarbon or unused polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample and monitored weekly for stability (See 7 6 3). Although not specifically required some typical calibration standard combinations follow when using those specific wavelengths listed in Table 1.

7 4 1 Mixed standard solution I—Manganese beryllium cadmium lead, and zinc

7 4 2 Mixed standard solution II—Barium copper iron vanadium and cobalt

7 4 3 Mixed standard solution III—Molybdenum silica arsenic and selenium

7 4 4 Mixed standard solution IV—Calcium sodium potassium aluminum chromium and nickel

7 4 5 Mixed standard solution V—Antimony, boron, magnesium, silver and thallium

NOTE 1 If the addition of silver to the recommended acid combination results in an initial precipitation add 15 mL of deionized distilled water and warm the flask until the solution clears. Cool and dilute to 100 mL with deionized distilled water. For this acid combination the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap water matrix for 30 days. Higher concentrations of silver require additional HCl.

7 5 Two types of blanks are required for the analysis. The calibration blank (3 13) is used in establishing the analytical curve while the reagent blank (3 12) is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

7 5 1 The calibration blank is prepared by diluting 2 mL of (1-1) HNO_3 and 10 mL of (1-1) HCl to 100 mL with deionized distilled water. (See Note 6.) Prepare a sufficient quantity to be used to flush the system between standards and samples.

7 5 2 The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

7 6 In addition to the calibration standards, an instrument check standard (3 7), an interference check sample (3 8) and a quality control sample (3 9) are also required for the analyses.

7 6 1 The instrument check standard is prepared by the analyst by combining compatible elements at a concentration equivalent to the midpoint of their respective calibration curves. (See 12 1 1.)

7 6 2 The interference check sample is prepared by the analyst in the following manner. Select a representative sample which contains minimal concentrations of the analytes of interest by known concentration of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at the approximate concentration of either 100 $\mu\text{g/L}$ or 5 times the estimated

detection limits given in Table 1. (For effluent samples of expected high concentrations, spike at an appropriate level.) If the type of samples analyzed are varied, a synthetically prepared sample may be used if the above criteria and intent are met. A limited supply of a synthetic interference check sample will be available from the Quality Assurance Branch of EMSL, Cincinnati. (See 12 1 2.)

7 6 3 The quality control sample should be prepared in the same acid matrix as the calibration standards at a concentration near 1 mg/L and in accordance with the instructions provided by the supplier. The Quality Assurance Branch of EMSL-Cincinnati will either supply a quality control sample or information where one of equal quality can be procured. (See 12 1 3.)

8. Sample handling and preservation

8 1 For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. Laboratory glassware including the sample bottle (whether polyethylene, polypropylene or FEP-fluorocarbon) should be thoroughly washed with detergent and tap water, rinsed with (1+1) nitric acid, tap water, (1+1) hydrochloric acid, tap and finally deionized, distilled water in that order. (See Notes 2 and 3.)

NOTE 2 Chromic acid may be useful to remove organic deposits from glassware, however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product, NOCHROMIX, available from Godax Laboratories, 6 Varick St., New York, NY 10013, may be used in place of chromic acid. Chromic acid should not be used with plastic bottles.

NOTE 3 If it can be documented through

an active analytical quality control program using spiked samples and reagent blanks that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

8 2 Before collection of the sample a decision must be made as to the type of data desired: that is, dissolved, suspended or total, so that the appropriate preservation and pretreatment steps may be accomplished. Filtration, acid preservation, etc., are to be performed at the time the sample is collected or as soon as possible thereafter.

8 2 1 For the determination of dissolved elements the sample must be filtered through a 0.45- μm membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus are recommended to avoid possible contamination.) Use the first 50-100 mL to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1-1) HNO_3 to a pH of 2 or less. Normally, 3 mL of (1-1) acid per liter should be sufficient to preserve the sample.

8 2 2 For the determination of suspended elements a measured volume of unpreserved sample must be filtered through a 0.45- μm membrane filter as soon as practical after collection. The filter plus suspended material should be transferred to a suitable container for storage and/or shipment. No preservative is required.

8 2 3 For the determination of total or total recoverable elements, the sample is acidified with (1-1) HNO_3 to pH 2 or less as soon as possible, preferable at the time of collection. The sample is not filtered before processing.

9. Sample Preparation

9 1 For the determinations of dissolved elements, the filtered, preserved sample may often be analyzed as received. The acid matrix and concentration of the samples and calibration standards must be the same. (See Note 6.) If a precipitate formed upon acidification of the sample or during transit or storage, it must be redissolved before the analysis by adding additional acid and/or by heat as described in 9 3.

9 2 For the determination of suspended elements, transfer the membrane filter containing the insoluble material to a 150-mL Griffin beaker and add 4 mL conc. HNO_3 . Cover the

beaker with a watch glass and heat gently. The warm acid will soon dissolve the membrane.

Increase the temperature of the hot plate and digest the material. When the acid has nearly evaporated, cool the beaker and watch glass and add another 3 mL of conc. HNO_3 . Cover and continue heating until the digestion is complete, generally indicated by a light colored digestate. Evaporate to near dryness (2 mL), cool, add 10 mL HCl (1-1) and 15 mL deionized distilled water per 100 mL dilution and warm the beaker gently for 15 min. to dissolve any precipitated or residue material. Allow to cool, wash down the watch glass and beaker walls with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the volume based on the expected concentrations of elements present. This volume will vary depending on the elements to be determined. (See Note 6.) The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended".

NOTE 4. In place of filtering, the sample after diluting and mixing may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

9.3 For the determination of total elements, choose a measured, volume of the well mixed acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker. (See Note 5.) Add 3 mL of conc. HNO_3 . Place the beaker on a hot plate and evaporate to near dryness cautiously, making certain that the sample does not boil and that no area of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 5 mL portion of conc. HNO_3 . Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing.) Again, evaporate to near dryness and cool the beaker. Add 10 mL of 1-1 HCl and 15 mL of deionized distilled water per 100 mL of final solution and warm the beaker gently for 15 min. to dissolve any precipitate or residue resulting from evaporation. Allow to cool, wash down the beaker walls and watch glass with deionized distilled water and filter the sample to remove insoluble material that could

clog the nebulizer. (See Note 4.) Adjust the sample to a predetermined volume based on the expected concentrations of elements present. The sample is now ready for analysis. (See Note 6.) Concentrations so determined shall be reported as "total".

NOTE 5. If low determinations of boron are critical, quartz glassware should be used.

NOTE 6. If the sample analysis solution has a different acid concentration from that given in 9.4 but does not introduce a physical interference or affect the analytical result, the same calibration standards may be used.

9.4 For the determination of total recoverable elements, choose a measured volume of a well mixed, acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker. (See Note 5.) Add 2 mL of (1-1) HNO_3 and 10 mL of (1-1) HCl to the sample and heat on a steam bath or hot plate until the volume has been reduced to near 25 mL, making certain the sample does not boil. After this treatment, cool the sample and filter to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the volume to 100 mL and mix. The sample is now ready for analysis. Concentrations so determined shall be reported as "total".

10. Procedure

10.1 Set up instrument with proper operating parameters established in 6.2. The instrument must be allowed to become thermally stable before beginning. This usually requires at least 30 min. of operation prior to calibration.

10.2 Initiate appropriate operating configuration of computer.

10.3 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in 7.4. Flush the system with the calibration blank (7.5.1) between each standard. (See Note 7.) (The use of the average intensity of multiple exposures for both standardization and sample analysis has been found to reduce random error.)

NOTE 7. For boron concentrations greater than 500 $\mu\text{g/L}$, extended flush times of 1 to 2 min. may be required.

10.4 Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a

sample. Concentration values obtained should not deviate from the actual values by more than ± 5 percent (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

10.5 Begin the sample run flushing the system with the calibration blank solution (7.5.1) between each sample. (See Note 7.) Analyze the instrument check standard (7.6.1) and the calibration blank (7.5.1) each 10 samples.

10.6 If it has been found that method of standard addition is required, the following procedure is recommended.

10.6.1 The standard addition technique (14.2) involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interference which causes a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows: Two identical aliquots of the sample solution, each of volume V_x , are taken. To the first (labeled A) is added a small volume V_s of a standard analyte solution of concentration c_s . To the second (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration c_x is calculated:

$$c_x = \frac{S_B V_s c_s}{(S_A - S_B) V_x}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and c_s should be chosen so that S_A is roughly twice S_B on the average. It is best if V_s is made much less than V_x , and thus c_s is much greater than c_x , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results from this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same as the analyte in the sample.

3 The interference effect must be constant over the working range of concern

4 The signal must be corrected for any additive interference

11. Calculation

11.1 Reagent blanks (7.5.2) should be subtracted from all samples. This is particularly important for digested samples requiring large quantities of acids to complete the digestion

11.2 If dilutions were performed, the appropriate factor must be applied to sample values

11.3 Data should be rounded to the thousandth place and all results should be reported in mg/L up to three significant figures

12. Quality Control (Instrumental)

12.1 Check the instrument standardization by analyzing appropriate quality control check standards as follow

12.1.1 Analyze an appropriate instrument check standard (7.6.1) containing the elements of interest at a frequency of 10%. This check standard is used to determine instrument drift. If agreement is not within $\pm 5\%$ of the expected values or within the established control limits, whichever is lower, the analysis is out of control. The analysis should be terminated, the problem corrected, and the instrument recalibrated.

Analyze the calibration blank (7.5.1) at a frequency of 10%. The result should be within the established control limits of two standard deviations of the mean value. If not, repeat the analysis two more times and average the three results. If the average is not within the control limit, terminate the analysis, correct the problem and recalibrate the instrument.

12.1.2 To verify interelement and background correction factors analyze the interference check sample (7.6.2) at the beginning, end, and at periodic intervals throughout the sample run. Results should fall within the established control limits of 1.5 times the standard deviation of the mean value. If not, terminate the analysis, correct the problem and recalibrate the instrument.

12.1.3 A quality control sample (7.6.3) obtained from an outside source must first be used for the initial verification of the calibration

standards. A fresh dilution of this sample shall be analyzed every week thereafter to monitor their stability. If the results are not within $\pm 5\%$ of the true value listed for the control sample, prepare a new calibration standard and recalibrate the instrument. If this does not correct the problem, prepare a new stock standard and a new calibration standard and repeat the calibration.

Precision and Accuracy

13.1 In an EPA round robin phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been dosed with various metal concentrates. Table 4 lists the true value, the mean reported value and the mean % relative standard deviation.

References

- 1 Winge, R. K., V. J. Peterson and V. A. Fassel, 'Inductively Coupled Plasma-Atomic Emission Spectroscopy Prominent Lines,' EPA-600/4-79-017
- 2 Winefordner, J. D., Trace Analysis Spectroscopic Methods for Elements, *Chemical Analysis*, Vol 46, pp 41-42
- 3 Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EPA-600/4-79-019
- 4 Garbarino, J. R. and Taylor, H. E., "An Inductively-Coupled Plasma Atomic Emission Spectrometric Method for Routine Water Quality Testing," *Applied Spectroscopy* 33, No 3(1979)
- 5 "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020
- 6 Annual Book of ASTM Standards, Part 31
- 7 "Carcinogens - Working With Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No 77-206, Aug 1977
- 8 "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976)
- 9 'Safety in Academic Chemistry Laboratories, American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979

Table 1 Recommended Wavelengths and Estimated Instrumental Detection Limits

<i>Element</i>	<i>Wavelength, nm</i>	<i>Estimated detection limit, $\mu\text{g/L}^2$</i>
Aluminum	308 215	45
Arsenic	193 696	53
Antimony	206 833	32
Barium	455 403	2
Beryllium	313 042	0.3
Boron	249 773	5
Cadmium	226 502	4
Calcium	317 933	10
Chromium	267 716	7
Cobalt	228 616	7
Copper	324 754	6
Iron	259 940	7
Lead	220 353	42
Magnesium	279 079	30
Manganese	257 610	2
Molybdenum	202 030	8
Nickel	231 604	15
Potassium	766 491	see ³
Selenium	196 026	75
Silica (SiO ₂)	288 158	58
Silver	328 068	7
Sodium	588 995	29
Thallium	190 864	40
Vanadium	292 402	8
Zinc	213 856	2

¹The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (See 5.1.1.)

²The estimated instrumental detection limits as shown are taken from "Inductively Coupled Plasma-Atomic Emission Spectroscopy-Prominent Lines," EPA-600/4-79-017. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

³Highly dependent on operating conditions and plasma position.

Table 2. Analyte Concentration Equivalents (mg/L) Arising From Interferents at the 100 mg/L Level

Analyte	Wavelength, nm	Interferent									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308 215	—	—	—	—	—	—	0 21	—	—	1 4
Antimony	206 833	0 47	—	2 9	—	0 08	—	—	—	25	0 45
Arsenic	193 696	1 3	—	0 44	—	—	—	—	—	—	1 1
Barium	455 403	—	—	—	—	—	—	—	—	—	—
Beryllium	313 042	—	—	—	—	—	—	—	—	0 04	0 05
Boron	249 773	0 04	—	—	—	0 32	—	—	—	—	—
Cadmium	226 502	—	—	—	—	0 03	—	—	0 02	—	—
Calcium	317 933	—	—	0 08	—	0 01	0 01	0 04	—	0 03	0 03
Chromium	267 716	—	—	—	—	0 003	—	0 04	—	—	0 04
Cobalt	228 616	—	—	0 03	—	0 005	—	—	0 03	0 15	—
Copper	324 754	—	—	—	—	0 003	—	—	—	0 05	0 02
Iron	259 940	—	—	—	—	—	—	0 12	—	—	—
Lead	220 353	0 17	—	—	—	—	—	—	—	—	—
Magnesium	279 079	—	0 02	0 11	—	0 13	—	0 25	—	0 07	0 12
Manganese	257 610	0 005	—	0 01	—	0 002	0 002	—	—	—	—
Molybdenum	202 030	0 05	—	—	—	0 03	—	—	—	—	—
Nickel	231 604	—	—	—	—	—	—	—	—	—	—
Selenium	196 026	0 23	—	—	—	0 09	—	—	—	—	—
Silicon	288 158	—	—	0 07	—	—	—	—	—	—	0 01
Sodium	588 995	—	—	—	—	—	—	—	—	0 08	—
Thallium	190 864	0 30	—	—	—	—	—	—	—	—	—
Vanadium	292 402	—	—	0 05	—	0 005	—	—	—	0 02	—
Zinc	213 856	—	—	—	0 14	—	—	—	0 29	—	—

Table 3 Interferent and Analyte Elemental Concentrations Used for Interference Measurements in Table 2

Analytes	(mg/L)	Interferents	(mg/L)
Al	10	Al	1000
As	10	Ca	1000
B	10	Cr	200
Ba	1	Cu	200
Be	1	Fe	1000
Ca	1	Mg	1000
Cd	10	Mn	200
Co	1	Ni	200
Cr	1	Ti	200
Cu	1	V	200
Fe	1		
Mg	1		
Mn	1		
Mo	10		
Na	10		
Ni	10		
Pb	10		
Sb	10		
Se	10		
Si	1		
Ti	10		
V	1		
Zn	10		

Table 4 ICP Precision and Accuracy Data

Element	Sample # 1			Sample #2			Sample #3		
	True Value µg/L	Mean Reported Value µg/L	Mean Percent RSD	True Value µg/L	Mean Reported Value µg/L	Mean Percent RSD	True Value µg/L	Mean Reported Value µg/L	Mean Percent RSD
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
V	750	749	1.8	70	69	2.9	170	169	1.1
As	200	208	7.5	22	19	23	60	63	17
Cr	150	149	3.8	10	10	18	50	50	3.3
Cu	250	235	5.1	11	11	40	70	67	7.9
Fe	600	594	3.0	20	19	15	180	178	6.0
Al	700	696	5.6	60	62	33	160	161	13
Cd	50	48	12	2.5	2.9	16	14	13	16
Co	500	512	10	20	20	4.1	120	108	21
Ni	250	245	5.8	30	28	11	60	55	14
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se	40	32	21.9	6	8.5	42	10	8.5	8.3

Not all elements were analyzed by all laboratories

ANTIMONY

Method 204.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01097

Dissolved 01095

Suspended 01096

Optimum Concentration Range: 20–300 ug/l

Detection Limit: 3 ug/l

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.2% (v/v) HNO₃.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.3 of the Atomic Absorption Methods section of this manual should be followed including the addition of sufficient 1:1 HCl to dissolve the digested residue for the analysis of suspended or total antimony. The sample solutions used for analysis should contain 2% (v/v) HNO₃.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–800°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 217.6 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. If chloride concentration presents a matrix problem or causes a loss previous to atomization, add an excess of 5 mg of ammonium nitrate to the furnace and ash using a ramp accessory or with incremental steps until the recommended ashing temperature is reached.
5. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
6. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
7. Data to be entered into STORET must be reported as ug/l.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

ARSENIC

Method 206.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01002

Dissolved 01000

Suspended 01001

Optimum Concentration Range: 5–100 $\mu\text{g/l}$

Detection Limit: 1 $\mu\text{g/l}$

Preparation of Standard Solution

1. Stock solution: Dissolve 1.320 g of arsenic trioxide, As_2O_3 (analytical reagent grade) in 100 ml of deionized distilled water containing 4 g NaOH. Acidify the solution with 20 ml conc. HNO_3 and dilute to 1 liter. 1 ml = 1 mg As (1000 mg/l).
2. Nickel Nitrate Solution, 5%. Dissolve 24.780 g of ACS reagent grade $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in deionized distilled water and make up to 100 ml.
3. Nickel Nitrate Solution, 1%. Dilute 20 ml of the 5% nickel nitrate to 100 ml with deionized distilled water.
4. Working Arsenic Solution. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, add 1 ml of conc. HNO_3 , 2 ml of 30% H_2O_2 and 2 ml of the 5% nickel nitrate solution. Dilute to 100 ml with deionized distilled water.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Transfer 100 ml of well-mixed sample to a 250 ml Griffin beaker, add 2 ml of 30% H_2O_2 and sufficient conc. HNO_3 to result in an acid concentration of 1% (v/v). Heat for 1 hour at 95°C or until the volume is slightly less than 50 ml.
2. Cool and bring back to 50 ml with deionized distilled water.
3. Pipet 5 ml of this digested solution into a 10-ml volumetric flask, add 1 ml of the 1% nickel nitrate solution and dilute to 10 ml with deionized distilled water. The sample is now ready for injection into the furnace.

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NOTE: If solubilization or digestion is not required, adjust the HNO_3 concentration of the sample to 1% (v/v) and add 2 ml of 30% H_2O_2 and 2 ml of 5% nickel nitrate to each 100 ml of sample. The volume of the calibration standard should be adjusted with deionized distilled water to match the volume change of the sample.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1100°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 193.7 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 μl injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
4. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
5. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as $\mu\text{g/l}$.

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent containing 15 $\mu\text{g/l}$ and spiked with concentrations of 2, 10 and 25 $\mu\text{g/l}$, recoveries of 85%, 90% and 88% were obtained respectively. The relative standard deviation at these concentrations levels were $\pm 8.8\%$, $\pm 8.2\%$, $\pm 5.4\%$ and $\pm 8.7\%$, respectively.
2. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 20, 50 and 100 $\mu\text{g As/l}$, the standard deviations were ± 0.7 , ± 1.1 and ± 1.6 respectively. Recoveries at these levels were 105%, 106% and 101%, respectively.

MERCURY
Method 245.1 (Manual Cold Vapor Technique)

STORET NO. Total 71900

Dissolved 71890

Suspended 71895

1. **Scope and Application**
 - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
 - 1.2 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the cold vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in or spiked to a natural system. For distilled water the heat step is not necessary.
 - 1.3 The range of the method may be varied through instrument and/or recorder expansion. Using a 100 ml sample, a detection limit of 0.2 ug Hg/l can be achieved; concentrations below this level should be reported as < 0.2 (see Appendix 11.2).
2. **Summary of Method**
 - 2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.
3. **Sample Handling and Preservation**
 - 3.1 Until more conclusive data are obtained, samples should be preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection. If only dissolved mercury is to be determined, the sample should be filtered through an all glass apparatus before the acid is added. For total mercury the filtration is omitted.
4. **Interference**
 - 4.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/l of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water.

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Issued 1974

- 4.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/l had no effect on recovery of mercury from spiked samples.
- 4.3 Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 ml). During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation of 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 ml). In addition, the dead air space in the BOD bottle must be purged before the addition of stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from sea water using this technique.
- 4.4 Interference from certain volatile organic materials which will absorb at this wavelength is also possible. A preliminary run without reagents should determine if this type of interference is present (see Appendix 11.1).

5. Apparatus

- 5.1 Atomic Absorption Spectrophotometer: (See Note 1) Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.
Note 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.
- 5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.
- 5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.
- 5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. X 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2" by 2" cards. One inch diameter holes are cut in the middle of each card; the cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.
- 5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.
- 5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.
- 5.7 Aeration Tubing: A straight glass frit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.
- 5.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (see Note 2). The apparatus is assembled as shown in Figure 1.

NOTE 2: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

6.1 Sulfuric Acid, Conc.. Reagent grade.

6.1.1 Sulfuric acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1.0 liter.

6.2 Nitric Acid, Conc: Reagent grade of low mercury content (See Note 3).

NOTE 3: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

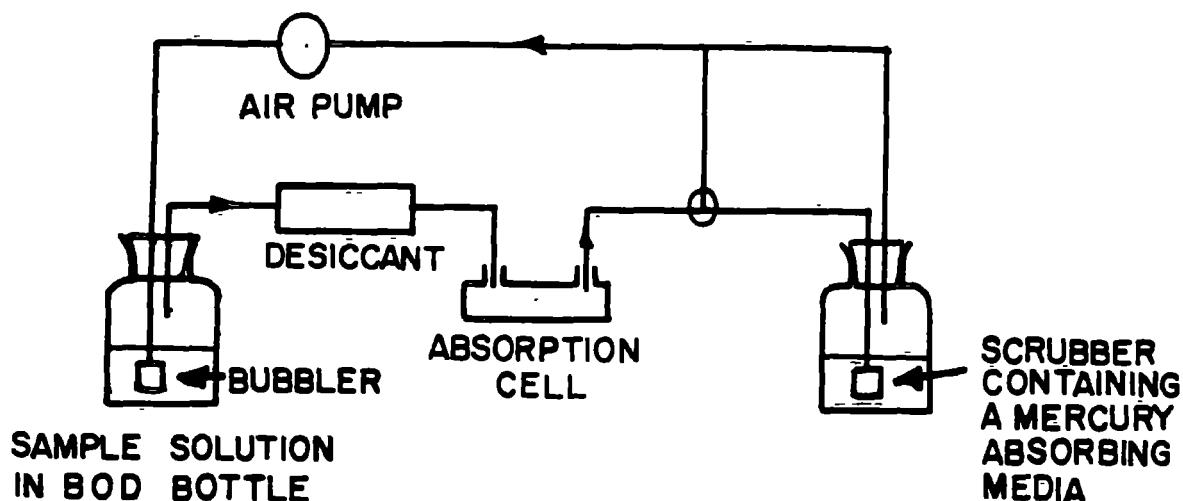
6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 ml. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 ml of distilled water.

6.6 Potassium Persulfate: 5% solution, w/v. Dissolve 5 g of potassium persulfate in 100 ml of distilled water.

6.7 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml of conc. nitric acid and adjust the volume to 100.0 ml. 1 ml = 1 mg Hg.



**FIGURE 1. APPARATUS FOR FLAMELESS
MERCURY DETERMINATION**

6.8 **Working Mercury Solution:** Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 μg per ml. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. **Calibration**

7.1 Transfer 0, 0.5, 1.0, 2.0, 5.0 and 10.0 ml aliquots of the working mercury solution containing 0 to 1.0 μg of mercury to a series of 300 ml BOD bottles. Add enough distilled water to each bottle to make a total volume of 100 ml. Mix thoroughly and add 5 ml of conc. sulfuric acid (6.1) and 2.5 ml of conc. nitric acid (6.2) to each bottle. Add 15 ml of KMnO_4 (6.5) solution to each bottle and allow to stand at least 15 minutes. Add 8 ml of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath maintained at 95°C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. When the solution has been decolorized wait 30 seconds, add 5 ml of the stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus forming a closed system. At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously (See Note 4). The absorbance will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 5). Close the bypass valve, remove the stopper and frit from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 4: An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

- a) equal volumes of 0.1 M KMnO_4 and 10% H_2SO_4
- b) 0.25% iodine in a 3% KI solution

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave. and N. Cassidy St., Columbus, Ohio 43219, Cat. #580-13 or #580-22.

8. **Procedure**

8.1 Transfer 100 ml, or an aliquot diluted to 100 ml, containing not more than 1.0 μg of mercury, to a 300 ml BOD bottle. Add 5 ml of sulfuric acid (6.1) and 2.5 ml of conc. nitric acid (6.2) mixing after each addition. Add 15 ml of potassium permanganate solution (6.5) to each sample bottle. For sewage samples additional permanganate may be required. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Add 8 ml of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath at 95°C. Cool and add 6

ml of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate. After a delay of at least 30 seconds add 5 ml of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under Calibration.

9. Calculation

9.1 Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

9.2 Calculate the mercury concentration in the sample by the formula:

$$\mu\text{g Hg/l} = \left(\frac{\mu\text{g Hg in aliquot}}{\text{aliquot}} \right) \left(\frac{1,000}{\text{volume of aliquot in ml}} \right)$$

9.3 Report mercury concentrations as follows: Below 0.2 $\mu\text{g/l}$, <0.2; between 1 and 10 $\mu\text{g/l}$, one decimal; above 10 $\mu\text{g/l}$, whole numbers.

10. Precision and Accuracy

10.1 In a single laboratory (EMSL), using an Ohio River composite sample with a background mercury concentration of 0.35 $\mu\text{g/l}$, spiked with concentrations of 1.0, 3.0 and 4.0 $\mu\text{g/l}$, the standard deviations were ± 0.14 , ± 0.10 and ± 0.08 , respectively. Standard deviation at the 0.35 level was ± 0.16 . Percent recoveries at the three levels were 89, 87, and 87%, respectively.

10.2 In a joint EPA/ASTM interlaboratory study of the cold vapor technique for total mercury in water, increments of organic and inorganic mercury were added to natural waters. Recoveries were determined by difference. A statistical summary of this study follows:

Number of Labs	True Values $\mu\text{g/liter}$	Mean Value $\mu\text{g/liter}$	Standard Deviation $\mu\text{g/liter}$	Accuracy as % Bias
76	0.21	0.349	0.276	66
80	0.27	0.414	0.279	53
82	0.51	0.674	0.541	32
77	0.60	0.709	0.390	18
82	3.4	3.41	1.49	0.34
79	4.1	3.81	1.12	-7.1
79	8.8	8.77	3.69	-0.4
78	9.6	9.10	3.57	-5.2

11. Appendix

11.1 While the possibility of absorption from certain organic substances actually being present in the sample does exist, EMSL has not encountered such samples. This is mentioned only to caution the analyst of the possibility. A simple correction that may be used is as follows: If an interference has been found to be present (4.4), the sample should be analyzed both by using the regular procedure and again under oxidizing conditions only.

that is without the reducing reagents. The true mercury value can then be obtained by subtracting the two values.

- 11.2 If additional sensitivity is required, a 200 ml sample with recorder expansion may be used provided the instrument does not produce undue noise. Using a Coleman MAS-50 with a drying tube of magnesium perchlorate and a variable recorder, 2 mv was set to read full scale. With these conditions, and distilled water solutions of mercuric chloride at concentrations of 0.15, 0.10, 0.05 and 0.025 $\mu\text{g}/\text{l}$ the standard deviations were ± 0.027 , ± 0.006 , ± 0.01 and ± 0.004 . Percent recoveries at these levels were 107, 83, 84 and 96%, respectively.
- 11.3 Directions for the disposal of mercury-containing wastes are given in ASTM Standards, Part 31, "Water", p 349, Method D3223 (1976).

Bibliography

1. Kopp, J. F., Longbottom, M. C. and Lobring, L. B., "Cold Vapor Method for Determining Mercury", AWWA, vol 64, p. 20, Jan., 1972.
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D3223-73, p 343 (1976).
3. Standard Methods for the Examination of Water and Wastewater. 14th Edition, p 156 (1975).

SELENIUM

Method 270.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01147

Dissolved 01145

Suspended 01146

Optimum Concentration Range: 5–100 ug/l

Detection Limit: 2 ug/l

Preparation of Standard Solution

1. **Stock Selenium Solution:** Dissolve 0.3453 g of selenous acid (actual assay 94.6% H_2SeO_3) in deionized distilled water and make up to 200 ml. 1 ml = 1 mg Se (1000 mg/l).
2. **Nickel Nitrate Solution, 5%:** Dissolve 24.780 g of ACS reagent grade $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in deionized distilled water and make up to 100 ml.
3. **Nickel Nitrate Solution, 1%:** Dilute 20 ml of the 5% nickel nitrate to 100 ml with deionized distilled water.
4. **Working Selenium Solution:** Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, add 1 ml of conc. HNO_3 , 2 ml of 30% H_2O_2 and 2 ml of the 5% nickel nitrate solution. Dilute to 100 ml with deionized distilled water.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Transfer 100 ml of well-mixed sample to a 250 ml Griffin beaker, add 2 ml of 30% H_2O_2 and sufficient conc. HNO_3 to result in an acid concentration of 1%(v/v). Heat for 1 hour at 95°C or until the volume is slightly less than 50 ml.
2. Cool and bring back to 50 ml with deionized distilled water.
3. Pipet 5 ml of this digested solution into a 10-ml volumetric flask, add 1 ml of the 1% nickel nitrate solution and dilute to 10 ml with deionized distilled water. The sample is now ready for injection into the furnace. NOTE: If solubilization or digestion is not required adjust the HNO_3 concentration of the sample to 1% (v/v) and add 2 ml of 30% H_2O_2 and 2 ml of 5% nickel nitrate to each 100 ml of sample. The volume of the calibration standard should be adjusted with deionized distilled water to match the volume change of the sample.

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Instrument Parameters

1. Drying time and temperature: 30 sec @ 125°C
2. Charring time and temperature: 30 sec @ 1200°C
3. Atomizing time and temperature: 10 sec @ 2700°C
4. Purge Gas Atmosphere: Argon
5. Wavelength: 196.0 nm.
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Selenium analysis suffers interference from chlorides (> 800 mg/l) and sulfate (> 200 mg/l). For the analysis of industrial effluents and samples with concentrations of sulfate from 200 to 2000 mg/l, both samples and standards should be prepared to contain 1% nickel.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
6. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
7. Data to entered into STORET must be reported as ug/l.

Precision and Accuracy

1. Using a sewage treatment plant effluent containing <2 ug/l and spiked with a concentration of 20 ug/l, a recovery of 99% was obtained.
2. Using a series of industrial waste effluents spiked at a 50 ug/l level, recoveries ranged from 94 to 112%.
3. Using a 0.1% nickel nitrate solution as a synthetic matrix with selenium concentrations of 5, 10, 20, 40, 50, and 100 ug/l, relative standard deviations of 14.2, 11.6, 9.3, 7.2, 6.4 and 4.1%, respectively, were obtained at the 95% confidence level.

4. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 5, 10, and 20 $\mu\text{g Se/l}$, the standard deviations were ± 0.6 , ± 0.4 , and ± 0.5 , respectively. Recoveries at these levels were 92%, 98%, and 100%, respectively.

Reference:

"Determining Selenium in Water, Wastewater, Sediment and Sludge By Flameless Atomic Absorption Spectroscopy", Martin, T. D., Kopp, J. F. and Ediger, R. D. Atomic Absorption Newsletter 14, 109 (1975).



THALLIUM

Method 279.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01059

Dissolved 01057

Suspended 01058

Optimum Concentration Range: 5–100 $\mu\text{g/l}$

Detection Limit: 1 $\mu\text{g/l}$

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3 .

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3 .

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C
2. Ashing Time and Temp: 30 sec @ 400°C
3. Atomizing Time and Temp: 10 sec @ 2400°C
4. Purge Gas Atmosphere: Argon
5. Wavelength: 276.8 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as ug/l.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

CHLORIDE

Method 325.3 (Titrimetric, Mercuric Nitrate)

STORET NO. 00940

1. Scope and Application
 - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
 - 1.2 The method is suitable for all concentration ranges of chloride content; however, in order to avoid large titration volume, a sample aliquot containing not more than 10 to 20 mg Cl per 50 ml is used.
 - 1.3 Automated titration may be used.
2. Summary of Method
 - 2.1 An acidified sample is titrated with mercuric nitrate in the presence of mixed diphenylcarbazone-bromophenol blue indicator. The end point of the titration is the formation of the blue-violet mercury diphenylcarbazone complex.
3. Comments
 - 3.1 Anions and cations at concentrations normally found in surface waters do not interfere.
 - 3.2 Sulfite interference can be eliminated by oxidizing the 50 ml of sample solution with 0.5 to 1 ml of H_2O_2 .
4. Apparatus
 - 4.1 Standard laboratory titrimetric equipment including a 1 ml or 5 ml microburet with 0.01 ml graduations.
5. Reagents
 - 5.1 Standard sodium chloride, 0.025 N: Dissolve 1.4613 \pm 0.0002 g (dried at 600°C for 1 hour) in chloride-free water in a 1 liter volumetric flask and dilute to the mark.
 - 5.2 Nitric acid, HNO_3 solution (3 + 997)
 - 5.3 Sodium hydroxide solution, NaOH, (10 g/l)
 - 5.4 Hydrogen peroxide (30%), H_2O_2
 - 5.5 Hydroquinone solution (10 g/liter): Dissolve 1 g of purified hydroquinone in water in a 100 ml volumetric and dilute to the mark.
 - 5.6 Mercuric nitrate titrant (0.141 N): Dissolve 25 g $Hg(NO_3)_2 \cdot H_2O$ in 900 ml of distilled water acidified with 5.0 ml conc. HNO_3 in a 1 liter volumetric flask and dilute to the mark with distilled water. Filter if necessary. Standardize against standard sodium chloride solution (5.1) using procedure 6. Adjust to exactly 0.141 N and check. Store in a dark bottle. A 1.00 ml aliquot is equivalent to 5.00 mg of chloride.
 - 5.7 Mercuric nitrate titrant (0.025 N): Dissolve 4.2830 g $Hg(NO_3)_2 \cdot H_2O$ in 50 ml of distilled water acidified with 0.5 ml conc. HNO_3 (sp. gr. 1.42) in a 1 liter volumetric flask and dilute to the mark with distilled water. Filter if necessary. Standardize against standard

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sodium chloride solution (5.1) using procedure 6. Adjust to exactly 0.025 N and check. Store in a dark bottle.

- 5.8 Mercuric nitrate titrant (0.0141 N): Dissolve 2.4200 g $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in 25 ml of distilled water acidified with 0.25 ml of conc. HNO_3 (sp. gr. 1.42) in a 1 liter volumetric flask and dilute to the mark with distilled water. Filter if necessary. Standardize against standard sodium chloride solution (5.1) using procedure 6. Adjust to exactly 0.0141 N and check. Store in a dark bottle. A 1 ml aliquot is equivalent to 500 μg of chloride.
- 5.9 Mixed indicator reagent: Dissolve 0.5 g crystalline diphenylcarbazone and 0.05 g bromophenol blue powder in 75 ml 95% ethanol in a 100 ml volumetric flask and dilute to the mark with 95% ethanol. Store in brown bottle and discard after 6 months.
- 5.10 Alphazurine indicator solution: Dissolve 0.005 g of alphazurine blue-green dye in 95% ethanol or isopropanol in a 100 ml volumetric and dilute to the mark with 95% ethanol or isopropanol.

6. Procedure

- 6.1 Place 50 ml of sample in a vessel for titration. If the concentration is greater than 20 mg/l chloride, use 0.141 N mercuric nitrate titrant (5.6) in step 6.6 or dilute. If the concentration is less than 2.5 mg/l of chloride, use 0.0141 N mercuric nitrate titrant (5.8) in step 6.6, a 1 ml or 5 ml microburet, and determine an indicator blank on 50 ml chloride-free water using procedure 6.6. If the concentration is less than 0.1 mg/l of chloride concentrate an appropriate volume to 50 ml.
- 6.2 Add 5 to 10 drops of mixed indicator reagent (5.9), shake or swirl solution.
- 6.3 If a blue-violet or red color appears add HNO_3 solution (5.2) dropwise until the color changes to yellow.
- 6.4 If a yellow or orange color forms immediately on addition of the mixed indicator, add NaOH solution (5.3) dropwise until the color changes to blue-violet; then add HNO_3 solution (5.2) dropwise until the color changes to yellow.
- 6.5 Add 1 ml excess HNO_3 solution (5.2).
- 6.6 Titrate with 0.025 N mercuric nitrate titrant (5.7) until a blue-violet color persists throughout the solution. See 6.1 for choice of titrant normality. Alphazurine indicator solution (5.10) may be added with the indicator to sharpen the end point. This will change color shades. Practice runs should be made.
- 6.7 Additional steps to eliminate particular interferences:
 - 6.7.1 If chromate is present at < 100 mg/l and iron is not present, add some alphazurine indicator solution (5.10) and acidify to pH 3 (indicating paper). End point will then be an olive-purple color.
 - 6.7.2 If chromate is present at > 100 mg/l and iron is not present, add 2 ml of fresh hydroquinone solution (5.5).
 - 6.7.3 If ferric ion is present use volume containing no more than 2.5 mg of ferric ion or ferric ion plus chromate ion. Add 2 ml fresh hydroquinone solution (5.5).
 - 6.7.4 If sulfite ion is present, add 0.5 ml of H_2O_2 solution (5.4) to 50 ml sample and mix for 1 minute.

7. Calculation

$$\text{mg chloride/l} = \frac{(A - B)N \times 35.450}{\text{ml of sample}}$$

where:

A = ml titrant for sample

B = ml titrant for blank

N = normality mercuric nitrate titrant

$$\text{mg NaCl/l} = \text{mg chloride/l} \times 1.65$$

8. Precision and Accuracy

8.1 Forty two analysts in eighteen laboratories analyzed synthetic water samples containing exact increments of chloride, with the following results:

<u>Increment as Chloride mg/liter</u>	<u>Precision as Standard Deviation mg/liter</u>	<u>Bias. %</u>	<u>Accuracy as Bias, mg/liter</u>
17	1.54	+2.16	+0.4
18	1.32	+3.50	+0.6
91	2.92	+0.11	+0.1
97	3.16	-0.51	-0.5
382	11.70	-0.61	-2.3
398	11.80	-1.19	-4.7

(FWPCA Method Study 1, Mineral and Physical Analyses)

- 8.2 In a single laboratory (EMSL), using surface water samples at an average concentration of 34 mg Cl/l, the standard deviation was ± 1.0 .
- 8.3 A synthetic unknown sample containing 241 mg/l chloride, 108 mg/l Ca, 82 mg/l Mg, 3.1 mg/l K, 19.9 mg/l Na, 1.1 mg/l nitrate N, 0.25 mg/l nitrite N, 259 mg/l sulfate and 42.5 mg/l total alkalinity (contributed by NaHCO_3) in distilled water was analyzed in 10 laboratories by the mercurimetric method, with a relative standard deviation of 3.3% and a relative error of 2.9%.

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CYANIDE, TOTAL

Method 335.2 (Titrimetric; Spectrophotometric)

STORET NO. 00720

1. **Scope and Application**
 - 1.1 This method is applicable to the determination of cyanide in drinking, surface and saline waters, domestic and industrial wastes.
 - 1.2 The titration procedure using silver nitrate with p-dimethylamino-benzal-rhodanine indicator is used for measuring concentrations of cyanide exceeding 1 mg/l (0.25 mg/250 ml of absorbing liquid).
 - 1.3 The colorimetric procedure is used for concentrations below 1 mg/l of cyanide and is sensitive to about 0.02 mg/l.
2. **Summary of Method**
 - 2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or colorimetrically.
 - 2.2 In the colorimetric measurement the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridine-barbituric acid reagent. The absorbance is read at 620 nm when using pyridine-pyrazolone or 578 nm for pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.
 - 2.3 The titrimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.
3. **Definitions**
 - 3.1 Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.
4. **Sample Handling and Preservation**
 - 4.1 The sample should be collected in plastic or glass bottles of 1 liter or larger size. All bottles must be thoroughly cleansed and thoroughly rinsed to remove soluble material from containers.
 - 4.2 Oxidizing agents such as chlorine decompose most of the cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.06 g of ascorbic acid for each liter of sample volume.

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Technical Revision 1980

- 4.3 Samples must be preserved with 2 ml of 10 N sodium hydroxide per liter of sample ($\text{pH} \geq 12$) at the time of collection.
- 4.4 Samples should be analyzed as rapidly as possible after collection. If storage is required, the samples should be stored in a refrigerator or in an ice chest filled with water and ice to maintain temperature at 4°C .

5. Interferences

- 5.1 Interferences are eliminated or reduced by using the distillation procedure described in Procedure 8.1, 8.2 and 8.3.
- 5.2 Sulfides adversely affect the colorimetric and titration procedures. Samples that contain hydrogen sulfide, metal sulfides or other compounds that may produce hydrogen sulfide during the distillation should be distilled by the optional procedure described in Procedure 8.2. The apparatus for this procedure is shown in Figure 3.
- 5.3 Fatty acids will distill and form soaps under the alkaline titration conditions, making the end point almost impossible to detect.
 - 5.3.1 Acidify the sample with acetic acid (1 + 9) to pH 6.0 to 7.0.

Caution: This operation must be performed in the hood and the sample left there until it can be made alkaline again after the extraction has been performed.
 - 5.3.2 Extract with iso-octane, hexane, or chloroform (preference in order named) with a solvent volume equal to 20% of the sample volume. One extraction is usually adequate to reduce the fatty acids below the interference level. Avoid multiple extractions or a long contact time at low pH in order to keep the loss of HCN at a minimum. When the extraction is completed, immediately raise the pH of the sample to above 12 with NaOH solution.
- 5.4 High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation nitrate and nitrite will form nitrous acid which will react with some organic compounds to form oximes. These compounds formed will decompose under test conditions to generate HCN. The interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid.

6. Apparatus

- 6.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.
- 6.2 Microburet, 5.0 ml (for titration).
- 6.3 Spectrophotometer suitable for measurements at 578 nm or 620 nm with a 1.0 cm cell or larger.
- 6.4 Reflux distillation apparatus for sulfide removal as shown in Figure 3. The boiling flask same as 6.1. The sulfide scrubber may be a Wheaton Bubber #709682 with 29 42 joints, size 100 ml. The air inlet tube should not be fritted. The cyanide absorption vessel should be the same as the sulfide scrubber. The air inlet tube should be fritted.
- 6.5 Flow meter, such as Lab Crest with stainless steel float (Fisher 11-164-50).

7. Reagents

- 7.1 Sodium hydroxide solution, 1.25N: Dissolve 50 g of NaOH in distilled water, and dilute to 1 liter with distilled water.

- 7.2 Lead acetate: Dissolve 30 g of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2) \cdot 3\text{H}_2\text{O}$ in 950 ml of distilled water. Adjust the pH to 4.5 with acetic acid. Dilute to 1 liter.
- 7.5 Sulfuric acid; 18N: Slowly add 500 ml of concentrated H_2SO_4 to 500 ml of distilled water.
- 7.6 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in 1 liter of distilled water. Refrigerate this solution.
- 7.7 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 900 ml of distilled water. Standardize with 0.0192 N AgNO_3 . Dilute to appropriate concentration so that 1 ml = 1 mg CN.
- 7.8 Standard cyanide solution, intermediate: Dilute 100.0 ml of stock (1 ml = 1 mg CN) to 1000 ml with distilled water (1 ml = 100.0 ug).
- 7.9 Working standard cyanide solution: Prepare fresh daily by diluting 100.0 ml of intermediate cyanide solution to 1000 ml with distilled water and store in a glass stoppered bottle. 1 ml = 10.0 ug CN.
- 7.10 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g AgNO_3 crystals and drying to constant weight at 40°C. Weigh out 3.2647 g of dried AgNO_3 , dissolve in distilled water, and dilute to 1000 ml (1 ml = 1mg CN).
- 7.11 Rhodanine indicator: Dissolve 20 mg of p-dimethyl-amino-benzalrhodanine in 100 ml of acetone.
- 7.12 Chloramine T solution: Dissolve 1.0 g of white, water soluble Chloramine T in 100 ml of distilled water and refrigerate until ready to use. Prepare fresh daily.
- 7.13 Color Reagent — One of the following may be used:
 - 7.13.1 Pyridine-Barbituric Acid Reagent: Place 15 g of barbituric acid in a 250 ml volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 ml of pyridine and mix. Add 15 ml of conc. HCl, mix, and cool to room temperature. Dilute to 250 ml with distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.
 - 7.13.2 Pyridine-pyrazolone solution:
 - 7.13.2.1 3-Methyl-1-phenyl-2-pyrazolin-5-one reagent, saturated solution: Add 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 ml of distilled water, heat to 60°C with stirring. Cool to room temperature.
 - 7.13.2.2 3,3'-Dimethyl-1, 1'-diphenyl-[4,4'-bi-2 pyrazoline]-5,5'-dione (bispyrazolone): Dissolve 0.01 g of bispyrazolone in 10 ml of pyridine.
 - 7.13.2.3 Pour solution (7.13.2.1) through non-acid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution (7.13.2.2) collecting the filtrate in the same container as filtrate from (7.13.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with cyanide if used within 24 hours of preparation.
- 7.14 Magnesium chloride solution: Weigh 510 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ into a 1000 ml flask, dissolve and dilute to 1 liter with distilled water.
- 7.15 Sulfamic acid.

8. Procedure

8.1 For samples without sulfide.

- 8.1.1 Place 500 ml of sample, or an aliquot diluted to 500 ml in the 1 liter boiling flask. Pipet 50 ml of sodium hydroxide (7.1) into the absorbing tube. If the apparatus in Figure 1 is used, add distilled water until the spiral is covered. Connect the boiling flask, condenser, absorber and trap in the train. (Figure 1 or 2)
- 8.1.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately two bubbles of air per second enters the boiling flask through the air inlet tube. Proceed to 8.4.

8.2 For samples that contain sulfide.

- 8.2.1 Place 500 ml of sample, or an aliquot diluted to 500 ml in the 1 liter boiling flask. Pipet 50 ml of sodium hydroxide (7.1) to the absorbing tube. Add 25 ml of lead acetate (7.2) to the sulfide scrubber. Connect the boiling flask, condenser, scrubber and absorber in the train. (Figure 3) The flow meter is connected to the outlet tube of the cyanide absorber.
- 8.2.2 Start a stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately 1.5 liters per minute enters the boiling flask through the air inlet tube. The bubble rate may not remain constant while heat is being applied to the flask. It may be necessary to readjust the air rate occasionally. Proceed to 8.4.

8.3 If samples contain NO , and or NO_2 , add 2 g of sulfamic acid solution (7.15) after the air rate is set through the air inlet tube. Mix for 3 minutes prior to addition of H_2SO_4 .

8.4 Slowly add 50 ml 18N sulfuric acid (7.5) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 min. Pour 20 ml of magnesium chloride (7.14) into the air inlet and wash down with a stream of water.

8.5 Heat the solution to boiling. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

8.6 Drain the solution from the absorber into a 250 ml volumetric flask. Wash the absorber with distilled water and add the washings to the flask. Dilute to the mark with distilled water.

8.7 Withdraw 50 ml or less of the solution from the flask and transfer to a 100 ml volumetric flask. If less than 50 ml is taken, dilute to 50 ml with 0.25N sodium hydroxide solution (7.4). Add 15.0 ml of sodium phosphate solution (7.6) and mix.

8.7.1 Pyridine-barbituric acid method: Add 2 ml of chloramine T (7.12) and mix. See Note 1. After 1 to 2 minutes, add 5 ml of pyridine-barbituric acid solution (7.13.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes for color development then read absorbance at 578 nm in a 1 cm cell within 15 minutes.

8.7.2 Pyridine-pyrazolone method: Add 0.5 ml of chloramine T (7.12) and mix. See Note 1 and 2. After 1 to 2 minutes add 5 ml of pyridine-pyrazolone solution

(7.13.1) and mix. Dilute to mark with distilled water and mix again. After 40 minutes read absorbance at 620 nm in a 1 cm cell.

NOTE 1: Some distillates may contain compounds that have a chlorine demand. One minute after the addition of chloramine T, test for residual chlorine with KI-starch paper. If the test is negative, add an additional 0.5 ml of chlorine T. After one minute, recheck the sample.

NOTE 2: More than 0.5 ml of chloramine T will prevent the color from developing with pyridine-pyrazolone.

8.8 Standard curve for samples without sulfide.

8.8.1 Prepare a series of standards by pipeting suitable volumes of standard solution (7.9) into 250 ml volumetric flasks. To each standard add 50 ml of 1.25 N sodium hydroxide and dilute to 250 ml with distilled water. Prepare as follows:

ML of Working Standard Solution (1 ml = 10 µg CN)	Conc. µg CN per 250 ml
0	BLANK
1.0	10
2.0	20
5.0	50
10.0	100
15.0	150
20.0	200

8.8.2 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If distilled standards do not agree within $\pm 10\%$ of the undistilled standards the analyst should find the cause of the apparent error before proceeding.

8.8.3 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations.

8.8.4 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (7.8) or the working standard (7.9) to 500 ml of sample to insure a level of 20 µg/l. Proceed with the analysis as in Procedure (8.1.1).

8.9 Standard curve for samples with sulfide.

8.9.1 It is imperative that all standards be distilled in the same manner as the samples. Standards distilled by this method will give a linear curve, but as the concentration increases, the recovery decreases. It is recommended that at least 3 standards be distilled.

8.9.2 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations.

8.10 Titrimetric method.

- 8.10.1 If the sample contains more than 1 mg/l of CN, transfer the distillate or a suitable aliquot diluted to 250 ml, to a 500 ml Erlenmeyer flask. Add 10-12 drops of the benzalrhodanine indicator.
- 8.10.2 Titrate with standard silver nitrate to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.
- 8.10.3 The analyst should familiarize himself with the end point of the titration and the amount of indicator to be used before actually titrating the samples.

9. Calculation

- 9.1 If the colorimetric procedure is used, calculate the cyanide, in $\mu\text{g/l}$, in the original sample as follows:

$$\text{CN, } \mu\text{g/l} = \frac{A \times 1,000}{B} \times \frac{50}{C}$$

where:

- A = μg CN read from standard curve
- B = ml of original sample for distillation
- C = ml taken for colorimetric analysis

9.2 Using the titrimetric procedure, calculate concentration of CN as follows:

$$\text{CN, mg/l} = \frac{(A - B)1.000}{\text{ml orig. sample}} \times \frac{250}{\text{ml of aliquot titrated}}$$

where:

A = volume of AgNO₃ for titration of sample.

B = volume of AgNO₃ for titration of blank.

10. Precision and Accuracy

10.1 In a single laboratory (EMSL), using mixed industrial and domestic waste samples at concentrations of 0.06, 0.13, 0.28 and 0.62 mg/l CN, the standard deviations were ± 0.005 , ± 0.007 , ± 0.031 and ± 0.094 , respectively.

10.2 In a single laboratory (EMSL), using mixed industrial and domestic waste samples at concentrations of 0.28 and 0.62 mg/l CN, recoveries were 85% and 102%, respectively.

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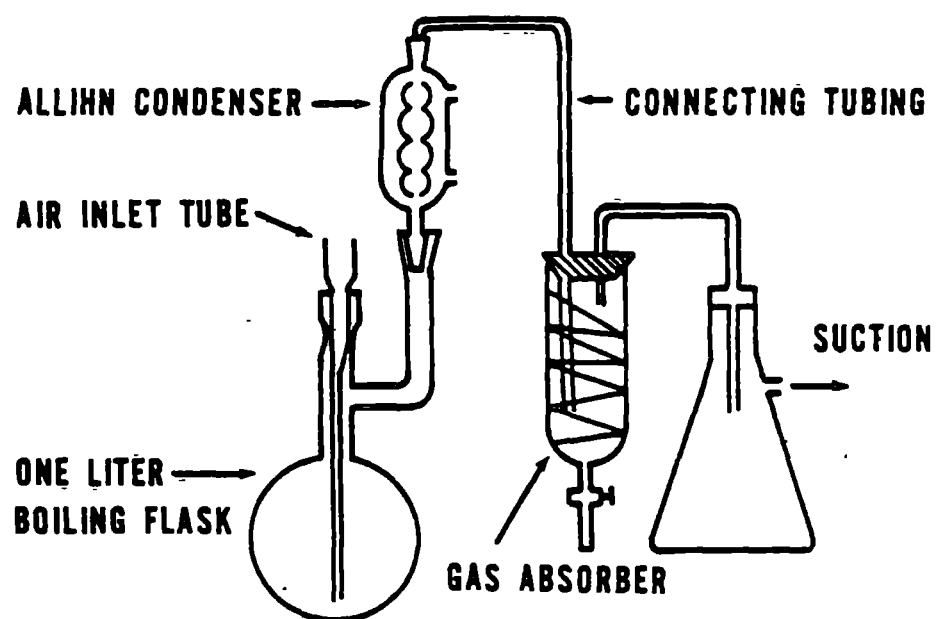


FIGURE 1
CYANIDE DISTILLATION APPARATUS

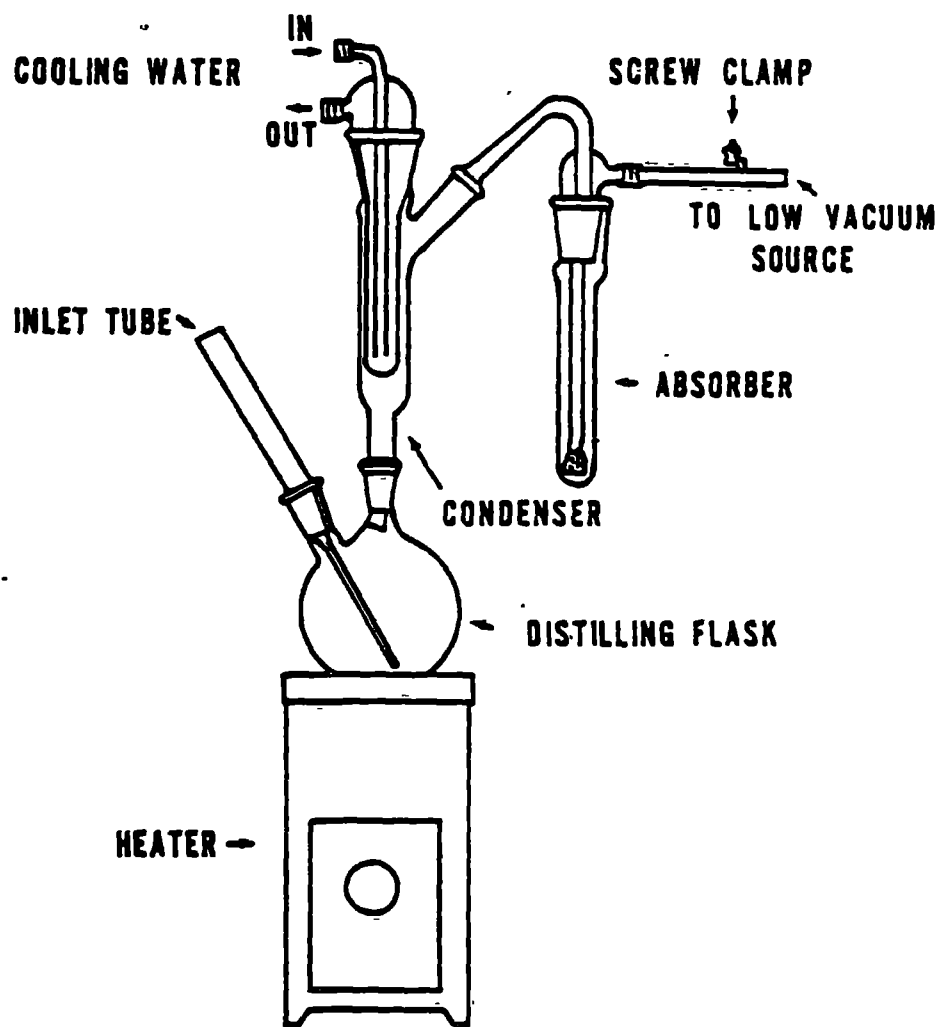


FIGURE 2
CYANIDE DISTILLATION APPARATUS

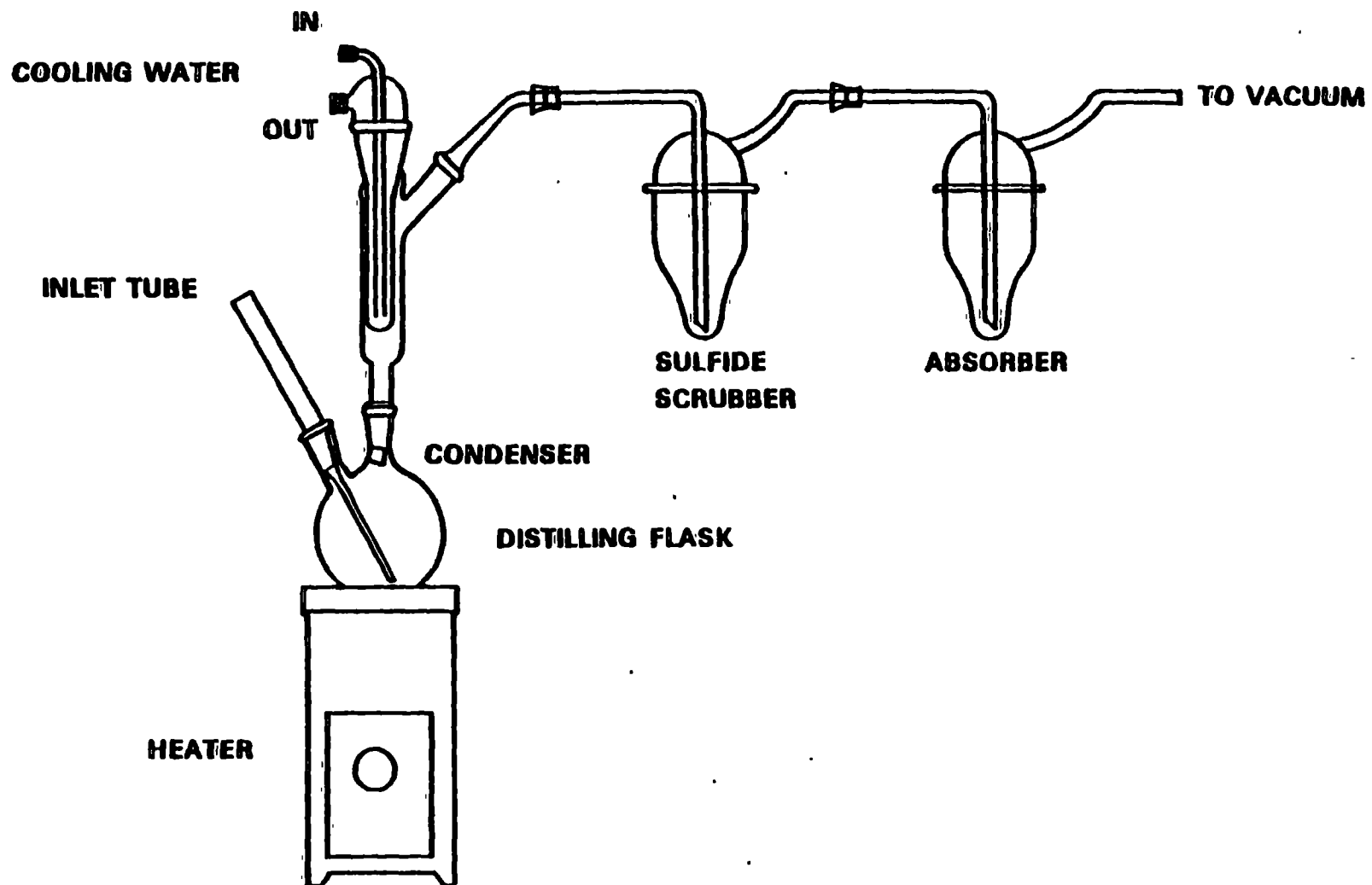


Figure 3.
Cyanide Distillation Apparatus

335.2-10

NITROGEN, AMMONIA

Method 350.2 (Colorimetric; Titrimetric; Potentiometric - Distillation Procedure)

STORET NO. Total 00610

Dissolved 00608

1. **Scope and Application**
 - 1.1 This distillation method covers the determination of ammonia-nitrogen exclusive of total Kjeldahl nitrogen, in drinking, surface and saline waters, domestic and industrial wastes. It is the method of choice where economics and sample load do not warrant the use of automated equipment.
 - 1.2 The method covers the range from about 0.05 to 1.0 mg $\text{NH}_3\text{-N/l}$ for the colorimetric procedure, from 1.0 to 25 mg/l for the titrimetric procedure, and from 0.05 to 1400 mg/l for the electrode method.
 - 1.3 This method is described for macro glassware; however, micro distillation equipment may also be used.
2. **Summary of Method**
 - 2.1 The sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is then distilled into a solution of boric acid. The ammonia in the distillate can be determined colorimetrically by nesslerization, titrimetrically with standard sulfuric acid with the use of a mixed indicator, or potentiometrically by the ammonia electrode. The choice between the first two procedures depends on the concentration of the ammonia.
3. **Sample Handling and Preservation**
 - 3.1 Samples may be preserved with 2 ml of conc. H_2SO_4 per liter and stored at 4°C.
4. **Interferences**
 - 4.1 A number of aromatic and aliphatic amines, as well as other compounds, both organic and inorganic, will cause turbidity upon the addition of Nessler reagent, so direct nesslerization (i.e., without distillation), has been discarded as an official method.
 - 4.2 Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent even at the pH of 9.5 at which distillation is carried out. Volatile alkaline compounds, such as certain ketones, aldehydes, and alcohols, may cause an off-color upon nesslerization in the distillation method. Some of these, such as formaldehyde, may be eliminated by boiling off at a low pH (approximately 2 to 3) prior to distillation and nesslerization.
 - 4.3 Residual chlorine must also be removed by pretreatment of the sample with sodium thiosulfate before distillation.

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5. Apparatus

- 5.1 An all-glass distilling apparatus with an 800–1000 ml flask.
- 5.2 Spectrophotometer or filter photometer for use at 425 nm and providing a light path of 1 cm or more.
- 5.3 Nessler tubes: Matched Nessler tubes (APHA Standard) about 300 mm long, 17 mm inside diameter, and marked at 225 mm \pm 1.5 mm inside measurement from bottom.
- 5.4 Erlenmeyer flasks: The distillate is collected in 500 ml glass-stoppered flasks. These flasks should be marked at the 350 and the 500 ml volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks.

6. Reagents

- 6.1 Distilled water should be free of ammonia. Such water is best prepared by passage through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.

NOTE 1: All solutions must be made with ammonia-free water.

- 6.2 Ammonium chloride, stock solution: 1.0 ml = 1.0 mg $\text{NH}_3\text{-N}$. Dissolve 3.819 g NH_4Cl in distilled water and bring to volume in a 1 liter volumetric flask.
- 6.3 Ammonium chloride, standard solution: 1.0 ml = 0.01 mg. Dilute 10.0 ml of stock solution (6.2) to 1 liter in a volumetric flask.
- 6.4 Boric acid solution (20 g/l): Dissolve 20 g H_3BO_3 in distilled water and dilute to 1 liter.
- 6.5 Mixed indicator: Mix 2 volumes of 0.2% methyl red in 95% ethyl alcohol with 1 volume of 0.2% methylene blue in 95% ethyl alcohol. This solution should be prepared fresh every 30 days.

NOTE 2: Specially denatured ethyl alcohol conforming to Formula 3A or 30 of the U.S. Bureau of Internal Revenue may be substituted for 95% ethanol.

- 6.6 Nessler reagent: Dissolve 100 g of mercuric iodide and 70 g of potassium iodide in a small amount of water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of NaOH in 500 ml of water. Dilute the mixture to 1 liter. If this reagent is stored in a Pyrex bottle out of direct sunlight, it will remain stable for a period of up to 1 year.

NOTE 3: This reagent should give the characteristic color with ammonia within 10 minutes after addition, and should not produce a precipitate with small amounts of ammonia (0.04 mg in a 50 ml volume).

- 6.7 Borate buffer: Add 88 ml of 0.1 N NaOH solution to 500 ml of 0.025 M sodium tetraborate solution (5.0 g anhydrous $\text{Na}_2\text{B}_4\text{O}_7$ or 9.5 g $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ per liter) and dilute to 1 liter.

- 6.8 Sulfuric acid, standard solution: (0.02 N, 1 ml = 0.28 mg $\text{NH}_3\text{-N}$). Prepare a stock solution of approximately 0.1 N acid by diluting 3 ml of conc. H_2SO_4 (sp. gr. 1.84) to 1 liter with CO_2 -free distilled water. Dilute 200 ml of this solution to 1 liter with CO_2 -free distilled water.

NOTE 4: An alternate and perhaps preferable method is to standardize the approximately 0.1 N H_2SO_4 solution against a 0.100 N Na_2CO_3 solution. By proper dilution the 0.02 N acid can then be prepared.

6.8.1 Standardize the approximately 0.02 N acid against 0.0200 N Na_2CO_3 solution. This last solution is prepared by dissolving 1.060 g anhydrous Na_2CO_3 , oven-dried at 140°C , and diluting to 1000 ml with CO_2 -free distilled water.

6.9 Sodium hydroxide, 1 N: Dissolve 40 g NaOH in ammonia-free water and dilute to 1 liter.

6.10 Dechlorinating reagents: A number of dechlorinating reagents may be used to remove residual chlorine prior to distillation. These include:

a. Sodium thiosulfate (1/70 N): Dissolve 3.5 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in distilled water and dilute to 1 liter. One ml of this solution will remove 1 mg/l of residual chlorine in 500 ml of sample.

b. Sodium arsenite (1/70 N): Dissolve 1.0 g NaAsO_2 in distilled water and dilute to 1 liter.

7. Procedure

7.1 Preparation of equipment: Add 500 ml of distilled water to an 800 ml Kjeldahl flask. The addition of boiling chips which have been previously treated with dilute NaOH will prevent bumping. Steam out the distillation apparatus until the distillate shows no trace of ammonia with Nessler reagent.

7.2 Sample preparation: Remove the residual chlorine in the sample by adding dechlorinating agent equivalent to the chlorine residual. To 400 ml of sample add 1 N NaOH (6.9), until the pH is 9.5, checking the pH during addition with a pH meter or by use of a short range pH paper.

7.3 Distillation: Transfer the sample, the pH of which has been adjusted to 9.5, to an 800 ml Kjeldahl flask and add 25 ml of the borate buffer (6.7). Distill 300 ml at the rate of 6–10 ml/min. into 50 ml of 2% boric acid (6.4) contained in a 500 ml Erlenmeyer flask.

NOTE 5: The condenser tip or an extension of the condenser tip must extend below the level of the boric acid solution.

Dilute the distillate to 500 ml with distilled water and nesslerize an aliquot to obtain an approximate value of the ammonia-nitrogen concentration. For concentrations above 1 mg/l the ammonia should be determined titrimetrically. For concentrations below this value it is determined colorimetrically. The electrode method may also be used.

7.4 Determination of ammonia in distillate: Determine the ammonia content of the distillate titrimetrically, colorimetrically or potentiometrically as described below.

7.4.1 Titrimetric determination: Add 3 drops of the mixed indicator to the distillate and titrate the ammonia with the 0.02 N H_2SO_4 , matching the end point against a blank containing the same volume of distilled water and H_3BO_3 solution.

7 4 2 Colorimetric determination: Prepare a series of Nessler tube standards as follows

<u>ml of Standard</u> <u>10 ml = 0.01 mg NH₃-N</u>	<u>mg NH₃-N/50.0 ml</u>
0.0	0.0
0.5	0.005
1.0	0.01
2.0	0.02
3.0	0.03
4.0	0.04
5.0	0.05
8.0	0.08
10.0	0.10

Dilute each tube to 50 ml with distilled water, add 2.0 ml of Nessler reagent (6.6) and mix. After 20 minutes read the absorbance at 425 nm against the blank. From the values obtained plot absorbance vs. mg NH₃-N for the standard curve. Determine the ammonia in the distillate by nesslerizing 50 ml or an aliquot diluted to 50 ml and reading the absorbance at 425 nm as described above for the standards. Ammonia-nitrogen content is read from the standard curve.

7 4 3 Potentiometric determination: Consult the method entitled Nitrogen, Ammonia, Selective Ion Electrode Method (Method 350.3) in this manual.

7 5 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If distilled standards do not agree with undistilled standards the operator should find the cause of the apparent error before proceeding.

8. Calculations

8 1 Titrimetric

$$\text{mg/l NH}_3 - \text{N} = \frac{A \times 0.28 \times 1,000}{S}$$

where:

A = ml 0.02 N H₂SO₄ used.

S = ml sample.

8.2 Spectrophotometric

$$\text{mg/l NH}_3 - \text{N} = \frac{A \times 1,000}{D} \times \frac{B}{C}$$

where:

A = mg NH₃-N read from standard curve.

B = ml total distillate collected, including boric acid and dilution.

C = ml distillate taken for nesslerization.

D = ml of original sample taken.

8.3 Potentiometric

$$\text{mg/l NH}_3\text{-N} = \frac{500}{D} \times A$$

where:

A = mg NH₃-N/l from electrode method standard curve.

D = ml of original sample taken

9. Precision and Accuracy

9.1 Twenty-four analysts in sixteen laboratories analyzed natural water samples containing exact increments of an ammonium salt, with the following results:

Increment as Nitrogen, Ammonia mg N/liter	Precision as Standard Deviation mgN/liter	Accuracy as	
		Bias, %	Bias, mg N/liter
0.21	0.122	-5.54	-0.01
0.26	0.070	-18.12	-0.05
1.71	0.244	+0.46	+0.01
1.92	0.279	-2.01	-0.04

(FWPCA Method Study 2, Nutrient Analyses)

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SULFATE

Method 375.4 (Turbidimetric)

STORET NO. Total 00945

1. **Scope and Application**
 - 1.1 This method is applicable to drinking and surface waters, domestic and industrial wastes.
 - 1.2 The method is suitable for all concentration ranges of sulfate; however, in order to obtain reliable readings, use a sample aliquot containing not more than 40 mg SO_4 /l.
 - 1.3 The minimum detectable limit is approximately 1 mg/l sulfate.
2. **Summary of Method**
 - 2.1 Sulfate ion is converted to a barium sulfate suspension under controlled conditions. The resulting turbidity is determined by a nephelometer, filter photometer or spectrophotometer and compared to a curve prepared from standard sulfate solutions.
 - 2.2 Suspended matter and color interfere. Correct by running blanks from which the barium chloride has been omitted.
 - 2.3 Silica in concentrations over 500 mg/l will interfere.
3. **Comments**
 - 3.1 Proprietary reagents, such as Hach Sulfaver or equivalent, are acceptable.
 - 3.2 Preserve by refrigeration at 4°C.
4. **Apparatus**
 - 4.1 Magnetic stirrer, variable speed so that it can be held constant just below splashing. Use identical shape and size magnetic stirring bars.
 - 4.2 Photometer: one of the following which are given in order of preference.
 - 4.2.1 Nephelometer
 - 4.2.2 Spectrophotometer for use at 420 nm with light path of 4 to 5 cm.
 - 4.2.3 Filter photometer with a violet filter having a maximum near 420 nm and a light path of 4 to 5 cm.
 - 4.3 Stopwatch, if the magnetic stirrer is not equipped with an accurate timer.
 - 4.4 Measuring spoon, capacity 0.2 to 0.3 ml.
5. **Reagents**
 - 5.1 Conditioning reagent: Place 30 ml conc. HCl, 300 ml distilled water, 100 ml 95% ethanol or isopropanol and 75 g NaCl in solution in a container. Add 50 ml glycerol and mix.
 - 5.2 Barium chloride, BaCl_2 , crystals, 20 to 30 mesh.
 - 5.3 Sodium carbonate solution (approximately 0.05N): Dry 3 to 5 g primary standard Na_2CO_3 at 250°C for 4 hours and cool in a desiccator. Weigh 2.5 \pm 0.2 g (to the nearest mg), transfer to a 1 liter volumetric flask and fill to the mark with distilled water.

Approved for NPDES
Issued 1971
Editorial revision 1978

5.4 Standard sulfate solution (1.00 ml = 100 μ g SO_4): Prepare by either 5.4.1 or 5.4.2.

5.4.1 Standard sulfate solution from H_2SO_4

5.4.1.1 Standard sulfuric acid, 0.1 N: dilute 3.0 ml conc. H_2SO_4 to 1 liter with distilled water. Standardize versus 40.00 ml of 0.05 N Na_2CO_3 solution (5.3) with about 60 ml distilled water by titrating potentiometrically to pH about 5. Lift electrodes and rinse into beaker. Boil gently for 3–5 minutes under a watch glass cover. Cool to room temperature. Rinse cover glass into beaker. Continue titration to the pH inflection point. Calculate normality using

$$N = \frac{A \times B}{53.00 \times C}$$

where:

A = g Na_2CO_3 weighed into 1 liter

B = ml Na_2CO_3 solution

C = ml acid used to inflection point

5.4.1.2 Standard acid, 0.02 N: Dilute appropriate amount of standard acid, 0.1 N (5.4.1.1) to 1 liter (200.00 ml if 0.1000 N). Check by standardization versus 15 ml of 0.05 N Na_2CO_3 solution (5.3).

5.4.1.3 Place 10.41 ml standard sulfuric acid, 0.02 N (5.4.1.2) in a 100 ml volumetric and dilute to the mark.

5.4.2 Standard sulfate solution from Na_2SO_4 : Dissolve 147.9 mg anhydrous Na_2SO_4 in distilled water in a 1 liter volumetric flask and dilute to the mark with distilled water.

6. Procedure

6.1 Formation of barium sulfate turbidity

6.1.1 Place 100 ml sample, or a suitable portion diluted to 100 ml, into a 250 Erlenmeyer flask.

6.1.2 Add exactly 5.0 ml conditioning reagent (5.1).

6.1.3 Mix in the stirring apparatus.

6.1.4 While the solution is being stirred, add a measuring spoonful of BaCl_2 crystals (5.2) and begin timing immediately.

6.1.5 Stir exactly 1.0 minutes at constant speed.

6.2 Measurement of barium sulfate turbidity

6.2.1 Immediately after the stirring period has ended, pour solution into absorbance cell.

6.2.2 Measure turbidity at 30 second intervals for 4 minutes.

6.2.3 Record the maximum reading obtained in the 4 minute period.

6.3 Preparation of calibration curve.

6.3.1 Prepare calibration curve using standard sulfate solution (5.4).

6.3.2 Space standards at 5 mg/l increments in the 0–40 mg/l sulfate range.

6.3.3 Above 50 mg/l the accuracy decreases and the suspensions lose stability.

6.3.4 Check reliability of calibration curve by running a standard with every 3 or 4 samples.

6.4 Correction for sample color and turbidity.

6.4.1 Run a sample blank using the procedure 6.1 and 6.2 without the addition of barium chloride (6.1.4).

7. Calculations

7.1 Read mg SO₄ from calibration curve

$$\text{mg SO}_4/\text{l} = \frac{\text{mg SO}_4 \times 1,000}{\text{ml sample}}$$

8. Precision and Accuracy

8.1 Thirty-four analysts in 16 laboratories analyzed six synthetic water samples containing exact increments of inorganic sulfate with the following results:

Increment as Sulfate mg/liter	Precision as Standard Deviation mg/liter	Accuracy as	
		Bias, %	Bias mg/liter
8.6	2.30	-3.72	-0.3
9.2	1.78	-8.26	-0.8
110	7.86	-3.01	-3.3
122	7.50	-3.37	-4.1
188	9.58	+0.04	+0.1
199	11.8	-1.70	-3.4

(FWPCA Method Study 1, Mineral and Physical Analyses).

8.2 A synthetic unknown sample containing 259 mg/l sulfate, 108 mg/l Ca, 82 mg/l Mg, 3.1 mg/l K, 19.9 mg/l Na, 241 mg/l chloride, 0.250 mg/l nitrite N, 1.1 mg/l nitrate N, and 42.5 mg/l total alkalinity (contributed by NaHCO₃) was analyzed in 19 laboratories by the turbidimetric method, with a relative standard deviation of 9.1% and a relative error of 1.2%.

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D516-68, Method B, p 430 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 496, Method 427C, (1975).



PHENOLICS, TOTAL RECOVERABLE

Method 420.1 (Spectrophotometric, Manual 4-AAP with Distillation)

STORET NO. 32730

1. **Scope and Application**
 - 1.1 This method is applicable to the analysis of drinking, surface and saline waters, domestic and industrial wastes.
 - 1.2 The method is capable of measuring phenolic materials at the 5 ug/l level when the colored end product is extracted and concentrated in a solvent phase using phenol as a standard.
 - 1.3 The method is capable of measuring phenolic materials that contain more than 50 ug/l in the aqueous phase (without solvent extraction) using phenol as a standard.
 - 1.4 It is not possible to use this method to differentiate between different kinds of phenols.
2. **Summary of Method**
 - 2.1 Phenolic materials react with 4-aminoantipyrine in the presence of potassium ferricyanide at a pH of 10 to form a stable reddish-brown colored antipyrine dye. The amount of color produced is a function of the concentration of phenolic material.
3. **Comments**
 - 3.1 For most samples a preliminary distillation is required to remove interfering materials.
 - 3.2 Color response of phenolic materials with 4-amino antipyrine is not the same for all compounds. Because phenolic type wastes usually contain a variety of phenols, it is not possible to duplicate a mixture of phenols to be used as a standard. For this reason phenol has been selected as a standard and any color produced by the reaction of other phenolic compounds is reported as phenol. This value will represent the minimum concentration of phenolic compounds present in the sample.
4. **Sample Handling and Preservation**
 - 4.1 Biological degradation is inhibited by the addition of 1 g/l of copper sulfate to the sample and acidification to a pH of less than 4 with phosphoric acid. The sample should be kept at 4°C and analyzed within 24 hours after collection.
5. **Interference**
 - 5.1 Interferences from sulfur compounds are eliminated by acidifying the sample to a pH of less than 4 with H_3PO_4 and aerating briefly by stirring and adding $CuSO_4$.
 - 5.2 Oxidizing agents such as chlorine, detected by the liberation of iodine upon acidification in the presence of potassium iodide, are removed immediately after sampling by the addition of an excess of ferrous ammonium sulfate (6.5). If chlorine is not removed, the phenolic compounds may be partially oxidized and the results may be low.

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6. Apparatus
 - 6.1 Distillation apparatus, all glass consisting of a 1 liter pyrex distilling apparatus with Graham condenser.
 - 6.2 pH meter.
 - 6.3 Spectrophotometer, for use at 460 or 510 nm.
 - 6.4 Funnels.
 - 6.5 Filter paper.
 - 6.6 Membrane filters.
 - 6.7 Separatory funnels, 500 or 1,000 ml.
 - 6.8 Nessler tubes, short or long form.
7. Reagents
 - 7.1 Phosphoric acid solution, 1 + 9: Dilute 10 ml of 85% H_3PO_4 to 100 ml with distilled water.
 - 7.2 Copper sulfate solution: Dissolve 100 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in distilled water and dilute to 1 liter.
 - 7.3 Buffer solution: Dissolve 16.9 g NH_4Cl in 143 ml conc. NH_4OH and dilute to 250 ml with distilled water. Two ml should adjust 100 ml of distillate to pH 10.
 - 7.4 Aminoantipyrine solution: Dissolve 2 g of 4AAP in distilled water and dilute to 100 ml.
 - 7.5 Potassium ferricyanide solution: Dissolve 8 g of $\text{K}_3\text{Fe}(\text{CN})_6$ in distilled water and dilute to 100 ml.
 - 7.6 Stock phenol solution: Dissolve 1.0 g phenol in freshly boiled and cooled distilled water and dilute to 1 liter. 1 ml = 1 mg phenol.
 - 7.7 Working solution A: Dilute 10 ml stock phenol solution to 1 liter with distilled water. 1 ml = 10 μg phenol.
 - 7.8 Working solution B: Dilute 100 ml of working solution A to 1000 ml with distilled water. 1 ml = 1 μg phenol.
 - 7.9 Chloroform
8. Procedure
 - 8.1 Distillation
 - 8.1.1 Measure 500 ml sample into a beaker. Lower the pH to approximately 4 with 1 + 9 H_3PO_4 (7.1), add 5 ml CuSO_4 solution (7.2) and transfer to the distillation apparatus. Omit adding H_2PO_4 and CuSO_4 if sample was preserved as described in 4.1.
 - 8.1.2 Distill 450 ml of sample, stop the distillation, and when boiling ceases add 50 ml of warm distilled water to the flask and resume distillation until 500 ml have been collected.
 - 8.1.3 If the distillate is turbid, filter through a prewashed membrane filter.
 - 8.2 Direct photometric method
 - 8.2.1 Using working solution A (7.7), prepare the following standards in 100 ml volumetric flasks.

<u>ml of working solution A</u>	<u>Conc. ug/l</u>
0	0.0
0.5	50.0
1.0	100.0
2.0	200.0
5.0	500.0
8.0	800.0
10.0	1000.0

8.2.2 To 100 ml of distillate or an aliquot diluted to 100 ml and/or standards, add 2 ml of buffer solution (7.3) and mix. The pH of the sample and standards should be 10 ± 0.2 .

8.2.3 Add 2.0 ml aminoantipyrine solution (7.4) and mix.

8.2.4 Add 2.0 ml potassium ferricyanide solution (7.5) and mix.

8.2.5 After 15 minutes read absorbance at 510 nm.

8.3 Chloroform extraction method

8.3.1 Using working solution B (7.8), prepare the following standards. Standards may be prepared by pipetting the required volumes into the separatory funnels and diluting to 500 ml with distilled water.

<u>ml of working solution B</u>	<u>Conc. ug/l</u>
0.0	0.0
3.0	6.0
5.0	10.0
10.0	20.0
20.0	40.0
25.0	50.0

8.3.2 Place 500 ml of distillate or an aliquot diluted to 500 ml in a separatory funnel. The sample should not contain more than 25 ug phenol.

8.3.3 To sample and standards add 10 ml of buffer solution (7.3) and mix. The pH should be 10 ± 0.2 .

8.3.4 Add 3.0 ml aminoantipyrine solution (7.4) and mix.

8.3.5 Add 3.0 ml potassium ferricyanide solution (7.5) and mix.

8.3.6 After three minutes, extract with 25 ml of chloroform (7.9). Shake the separatory funnel at least 10 times, let CHCl_3 settle, shake again 10 times and let chloroform settle again.

8.3.7 Filter chloroform extracts through filter paper. Do not add more chloroform.

8.3.8 Read the absorbance of the samples and standards against the blank at 460 nm.

9. Calculation

9.1 Prepare a standard curve by plotting the absorbance value of standards versus the corresponding phenol concentrations.

9.2 Obtain concentration value of sample directly from standard curve.

10. Precision and Accuracy

- 10.1 Using the extraction procedure for concentration of color, six laboratories analyzed samples at concentrations of 9.6, 48.3, and 93.5 $\mu\text{g}/\text{l}$. Standard deviations were ± 0.99 , ± 3.1 and $\pm 4.2 \mu\text{g}/\text{l}$, respectively.
- 10.2 Using the direct photometric procedure, six laboratories analyzed samples at concentrations of 4.7, 48.2 and 97.0 mg/l . Standard deviations were ± 0.18 , ± 0.48 and $\pm 1.58 \text{ mg}/\text{l}$, respectively.

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D1783-70, p553 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p574-581, Method 510 through 510C, (1975).

The following background and history of response actions is an excerpt from the MPCA Board Item on April 22, 1986 "Request for Approval of a Consent Decree with the Reilly Tar & Chemical Corporation and Other Parties for the Purpose of Completing Remedial Investigations and Feasibility Studies and Developing and Implementing Response Actions at and Around the Reilly Tar Site in St. Louis Park". This material is in Section I of the Issue Statement of that MPCA Board Item.

Between 1917 and 1972, Reilly Tar & Chemical Corporation (Reilly) operated a coal tar distillation and wood preserving plant, known as the Republic Creosote Company, in St. Louis Park. This plant was located on an 80 acre tract near State Highway 7 and Louisiana Avenue (the Reilly Site; Figure 1). Reilly disposed of wastewater from the operation in a network of ditches which discharged into a swamp south of the Reilly Site. In addition, the wood treating activities conducted on the Reilly Site resulted in creosote and coal tar contamination of the soils from drippings and spills. The major constituents of coal tar are phenolic compounds and polynuclear aromatic hydrocarbons (PAH). Some PAH compounds are carcinogenic, and are thus a source of concern when a municipal drinking water supply is contaminated with these compounds. (As used in the remainder of this board item, "contaminated" or "contamination" means PAH or phenolics are present in soil or ground water resulting from activities of Reilly at the Reilly Site.)

In 1932, the first municipal well in St. Louis Park (Old SLP #1) was constructed at Brunswick Avenue and West 36th Street, approximately one-half mile east of the Reilly Site. The well was finished in the Prairie du Chien-Jordan aquifer (Figure 2). After several weeks of operation, the well was closed due to taste and odor complaints (the taste was described as "swampy"). Laboratory tests showed that phenolic compounds were the apparent cause of the problem. Phenolics cause water to have an unpleasant taste and odor when the water is chlorinated, but these compounds are not believed to have adverse health effects at the low levels which cause the taste and odor problems.

Attempts to remedy the situation were unsuccessful, and the well was abandoned. Well drillers at the time speculated that the Reilly Site might be the source of the problem. Although Reilly, at the time, insisted that the problems at the municipal well were the result of "decaying vegetation" from the swamp south of the Reilly Site, it filled an unused well (W105) located on the Reilly Site with sand and extended the casings in Reilly's main water supply well (W23) to reduce interaquifer flow of possibly contaminated water.

Complaints from nearby residences over contamination of shallow wells and of odors from air emissions became more common, especially after extensive residential development of the area during the late 1940's into the 1950's. Because of continuing problems with soil and surface water contamination and odors 1/, the City of St. Louis Park (City) and the Minnesota Pollution Control Agency (MPCA) through the Attorney General (the State) filed suit against Reilly in 1970. In 1972, the City purchased the Reilly Site from Reilly, and

1/ See paragraph thirteen, page 9, of the attached Consent Decree for a listing of various studies and/or reports, chemical analysis and field investigations relating to the Reilly Site.

the plant was dismantled and removed. The City intended to use the property for a realignment of Louisiana Avenue and for residential development, and dropped its lawsuit against Reilly as a condition of the sale. However, the State did not drop the lawsuit, which is still pending and will be dismissed as part of the proposed settlement.

In 1974, the City contracted with Gerald Sunde, a consulting engineer, to investigate pathways for the movement of contaminants. Sunde concluded that wells in the area open to several aquifers (multi-aquifer wells) provide a significant pathway for the spread of contamination from contaminated surficial aquifers to deeper aquifers which would otherwise be protected from contamination by several bedrock layers. In 1975, the MPCA contracted with Barr Engineering to investigate subsurface contamination at and south of the Reilly Site. The results of this study showed significant contamination of soil and the surficial aquifer (the drift) with creosote. Because it appeared that Sunde's assessment of the pathways for contamination to deep aquifers was, at least in part, correct, the Minnesota Department of Health (MDH) in 1978 and 1979 contracted for the closure of 29 multi-aquifer wells in areas where the surficial aquifers were the most contaminated. In addition, the City and the U.S. Geological Survey installed a packer and casing in the former Reilly well, W23, to stop the extensive downhole flow of contaminated water into the Prairie du Chien - Jordan Aquifer.

Louisiana Avenue was constructed through the Reilly Site during the mid-1970's, and some multi-family housing units were constructed in the northern half of the Reilly Site during this same time period.

In 1978 the MDH began analyses of water from municipal supply wells in St. Louis Park and neighboring communities for PAH using high performance liquid chromatography. These and subsequent analyses led to the discovery of significant concentrations of PAH in six St. Louis Park wells and one Hopkins well, and these wells were shut down during the period 1978-81.

As a result of the determination that area ground water was contaminated the State amended, in 1978, its complaint in the lawsuit with Reilly to include claims for ground water contamination. All of the municipal wells cited above are finished in the Prairie du Chien-Jordan aquifer, which is the most heavily used aquifer for municipal drinking water supplies in the Twin Cities metropolitan area. The City of St. Louis Park has since overcome part of the resulting water supply shortfall through water conservation measures, installation of a new well in the Mt. Simon-Hinckley aquifer, and an interconnection with the City of Plymouth. In an attempt to understand the processes of contaminant transport in the Prairie du Chien-Jordan, the MDH and MPCA contributed toward a ground water flow and contaminant transport modeling study performed by the United States Geological Survey (USGS). In addition, the MDH funded a study by Hickok and Associates of the feasibility of ground water gradient control 2/ in 1981.

The MPCA received a \$400,000 grant from the U.S. Environmental Protection Agency (EPA) in December, 1981, and used this grant to finance a feasibility study conducted by the MPCA contractor, CH2M Hill, for replacement or treatment

2/ The term "gradient control", as used in this discussion, refers to the utilization of a pumping well or wells, usually located near the leading edge of the contamination plume, to control the flow of ground water in an aquifer to contain contamination within the area of control. It is in contrast to "source control", in which highly contaminated water is pumped at or near the source.

of the lost water supply; and to locate, investigate, and close multi-aquifer wells. In December, 1982, the EPA awarded the MPCA a \$1.99 million grant under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) to continue these studies, and to provide more funding for the USGS ground water modeling study for the purpose of designing a gradient control well system to control the movement of contaminants in the Prairie du Chien-Jordan aquifer.

The results of these studies have provided sufficient information to design a remedial approach for the contamination in the Prairie du Chien-Jordan aquifer. Multi-aquifer well investigation under the CERCLA grant has been limited to date, to two priority wells located on the Reilly Site. The most important of these, W23, was found to have a plug of coal tar in it, and has been cleaned out. The other well, W105, was the water supply well for the sugar beet plant which occupied the Reilly Site around the turn of the century, and was used by Reilly as a backup supply well until 1933. W105 was not found to be a source of contamination as was W23. The drinking water restoration study conducted by CH2M Hill, which analyzed the feasibility of various methods of treating drinking water, deeper wells, and an interconnection with Minneapolis, concluded that treatment with granular activated carbon (GAC) was the most cost-effective method of restoring the City's lost water supply. The USGS has completed its ground water flow modeling work, and this model has been used to examine gradient control schemes.

In September, 1980, the EPA filed suit against Reilly alleging violation of the Resource Conservation Recovery Act (RCRA). The State and St. Louis Park joined the lawsuit in October, 1980, followed by the City of Hopkins in June, 1981. After passage of CERCLA, the State filed an amended complaint in May, 1981, followed by St. Louis Park, the EPA, and Hopkins respectively in

August, September, and October, 1981. The State filed a second amended complaint under the Minnesota Environmental Response and Liability Act ("MERLA") in 1985 followed by St. Louis Park and Hopkins. In the event that agreement is not reached on the Consent Decree, the case is scheduled to be heard before U.S. District Court Judge Paul Magnuson.

In addition to the above litigation, Reilly filed a counterclaim against St. Louis Park, and St. Louis Park asserted a cross-claim against the State. Other parties involved with the purchase and development of the northern portion of the Reilly Site filed cross-claims against St. Louis Park and Reilly. 3/

In May, 1983, Reilly and its consultant, Environmental Research & Technology, Inc. (ERT) issued a report on the St. Louis Park ground water contamination. Discussion among MPCA, EPA, Reilly and ERT staff led to a period of negotiations toward a settlement. These talks broke down in early 1984.

Both the MPCA and EPA have instituted administrative action against Reilly, pursuant to the respective State and federal Superfund acts, in order to compel Reilly to undertake necessary remedial actions. The EPA issued a Record of Decision (ROD) in June, 1984 affirming that the most cost-effective remedy for restoring the City's lost water supply was installation of a GAC treatment system. In August, 1984, the EPA issued to Reilly an Administrative Order directing Reilly to design and construct the GAC system for City wells SLP 10 and 15 as provided in the ROD. In December, 1984, the MPCA issued a Request for Response Action (RFRA) to Reilly outlining a range of remedial investigations, feasibility studies, and necessary remedial actions.

3/ The following organizations were included as defendants in the lawsuit because they were involved with the purchase and development of the northern portion of the Reilly Site from St. Louis Park: Housing and Redevelopment Authority of St. Louis Park, Oak Park Village Associates, and Philips Investment Co.

Following these administrative actions, extensive negotiations, which had previously broken down, resumed among the MPCA, EPA, St. Louis Park, and Reilly in an effort to reach an effective settlement. General agreement on the terms and conditions of a proposed Consent Decree was reached in the Summer of 1985. However, because of its complex nature and the large number of parties involved, final agreement was delayed. Since the likelihood of settlement was always present, the MPCA staff did not return to the MPCA Board for further administrative actions.

Since general agreement regarding a Consent Decree had been reached in mid 1985, Reilly did proceed to design and construct a GAC system for City wells SLP 10 and 15. Reilly completed the construction of the GAC system in December, 1985 and the system is expected to be operational by May, 1986.

The following background and history of response actions is Part C of the Consent Decree. A list of relevant reference documents is included.

1. From 1917 until 1972, Reilly was engaged in the business of coal tar distillation and pressure treatment of wood products at its plant site at 7200 Walker Street, St. Louis Park, Hennepin County, Minnesota (hereinafter "the Site"). The Site encompassed an eighty (80) acre tract, which consists of Lot 1, Block 1; Lot 1, Block 2; Lot 1, Block 3; Lot 1, Block 4; Lot 1, Block 5; Lot 1, Block 6; Lot 1, Block 7; Lot 1, Block 8; Lot 1, Block 9; Lot 1, Block 10; all in Oak Park

Village according to the plat thereof on file in the office of the County Recorder of Hennepin County, Minnesota.

2. On or about October 2, 1970, the State, through its Pollution Control Agency, and St. Louis Park, filed a complaint in the Hennepin County District Court of the State of Minnesota alleging violations by Reilly of state and municipal pollution control laws and regulations. State of Minnesota by the Minnesota Pollution Control Agency, and the City of St. Louis Park v. Reilly Tar & Chemical Corporation, Hennepin County District Court, Civil File No. 670767 (hereinafter "Hennepin County Lawsuit").

3. On April 14, 1972, St. Louis Park agreed to purchase the Site from Reilly. The purchase agreement included a promise by St. Louis Park to obtain dismissals with prejudice by the State and by St. Louis Park of the Hennepin County Lawsuit. The purchase agreement also provided for acceptance by St. Louis Park of the property in an "as is" condition, including "any and all questions of soil and water impurities and soil conditions," and an agreement by St. Louis Park "to make no claim against Reilly for damages relative to soil and water impurities, if any, in any way relating to the premises sold herein, or relative to any other premises in which the City of St. Louis Park holds an interest. . . ."

4. A closing was scheduled on the property for June 19, 1973. However, the State did not execute a dismissal

of the Hennepin County Lawsuit. Accordingly, the City of St. Louis Park agreed that it would "hold Reilly harmless from any and all claims which may be asserted against it by the State of Minnesota, acting by and through the Minnesota Pollution Control Agency, and will be fully responsible for restoring the property, at its expense, to any condition that may be required by the Minnesota Pollution Control Agency". The City of St. Louis Park and Reilly executed and filed dismissals with prejudice of their claims in the Hennepin County Lawsuit, and the closing took place thereafter.

5. On June 21, 1973, the property was conveyed by quitclaim deed from St. Louis Park to the Housing and Redevelopment Authority of St. Louis Park, Minnesota, which thereafter conveyed part of the property to Oak Park Village Associates, Rustic Oaks Condominium, Inc. and Philip's Investment Co.

The Agreement for Purchase and Sale of Real Estate dated October 4, 1977 and the First Addendum to the Agreement dated October 6, 1977 between the St. Louis Park Housing and Redevelopment Authority and Diversified Equities Corporation [Oak Park Village Associates] regarding Lot 1, Block 3, Oak Park Village, Hennepin County, Minnesota, provides as follows:

14. Environmental Matters

The Agency [St. Louis Park Housing and Redevelopment Authority] shall prepare and shall incur all expenses for any environmental approvals, assessments, environmental impact

statements or such other environmental review documents deemed necessary or desirable by governmental authority.

Agency [St. Louis Park Housing and Redevelopment Authority] agrees to indemnify and save Redeveloper harmless from and against any and all loss or damage Redeveloper or successors may suffer from damage to improvements constructed on the Property as a result of claims, demands, costs or judgments against and arising out of soil or ground water contamination existing as of the date hereof, or caused by conditions existing as of the date hereof.

The Agreement for Purchase and Sale of Real Estate dated June 1, 1979 by and between the Housing and Redevelopment Authority of St. Louis Park and Ben Weber [Philip's Investment Co.] and the City of St. Louis Park regarding Lot 1, Block 6, Oak Park Village, Hennepin County, Minnesota, provides as follows:

14. Environmental Matters.

a. Both the City and the Redeveloper agree that the Stipulation between the City and the PCA dated April 19, 1977, is capable of a possible variety of interpretations. As between the Agency [St. Louis Park Housing and Redevelopment Authority], the City and the Redeveloper, as an inducement to the City and Agency to allow the Redeveloper to develop the Property and as security against the Redeveloper, or its assigns or successors in interest, claiming the right to benefit from a broader interpretation of said Stipulation and as an inducement to the Redeveloper to develop the Property and as security against the City or Agency claiming the right to benefit from a narrower interpretation of said Stipulation, the City, Agency and Redeveloper agree that, as between the parties to this Agreement, this paragraph 14 shall constitute the sole remedy available to Redeveloper against the City and Agency for any action or claim against or loss or damage to the

Redeveloper which is based on, derived from, or related to the soil or groundwater conditions of the Property, and shall constitute, as between the parties to this agreement, their interpretation of the Stipulation.

b. The City will not require the Redeveloper to excavate soil from the Property in question because of soil or groundwater contamination resulting from the operations of the former Republic Creosote Plant.

c. The City will indemnify the Redeveloper from damage consisting of physical destruction or injury to improvements on the property due solely to soil excavation on the Property required by public agencies. This indemnification shall not include consequential damage, lost income, lost profit or other forms of indirect loss or damage nor shall it include damage arising from personal injury. Indemnification shall be on a replacement cost less depreciation basis.

d. The indemnification granted by this agreement shall be secondary to any other rights or potential rights which the Redeveloper may have to compensation for any damage or loss whether through eminent domain, grants or otherwise. The Redeveloper shall exercise good faith effort to seek and obtain such compensation before presenting a claim under this indemnification agreement. Any compensation from any other source for damages indemnified herein shall reduce the indemnification liability of the City dollar per dollar.

e. This indemnification and agreement shall not be assignable except to the first mortgagee and shall terminate on January 1, 1985. All claims to indemnification under this agreement must be made in writing and received by the City Clerk of the City prior to January 2, 1985.

6. In April, 1978, the State moved to amend its complaint in the Hennepin County Lawsuit, alleging that PAH substances contained in Reilly's coal tar and creosote wastes had entered the ground water beneath the Site and that their

further migration threatened to contaminate aquifers relied on for public water supply. At the same time, St. Louis Park moved to intervene as a plaintiff. The motions were granted and interlocutory review was denied by the Minnesota Supreme Court. Reilly subsequently tendered defense of the action to St. Louis Park and counterclaimed against St. Louis Park, asserting that St. Louis Park was responsible for dealing with this problem under the hold harmless agreement made at the time of its purchase of the Site.

7. On or about September 4, 1980, the United States commenced this action by filing a complaint under Section 7003 of the Resource Conservation and Recovery Act ("RCRA"), 42 U.S.C. § 6973, alleging, inter alia, the existence of an imminent and substantial endangerment to health and the environment due to the handling, treatment, storage, transportation, disposal and presence of hazardous waste at the Site. On or about October 15, 1980, the State and St. Louis Park were granted leave to intervene in the RCRA Section 7003 claim and to assert additional claims under Minnesota law. On or about June 16, 1981, Hopkins was granted leave to intervene in the RCRA Section 7003 claim and to assert additional claims under Minnesota law.

8. On or about September 9, 1981, the United States filed an amended complaint, alleging in addition to the RCRA § 7003 claim, claims under Sections 106 and 107 of the

Comprehensive Environmental Response, Compensation and Liability Act ("CERCLA"), 42 U.S.C. §§ 9606 and 9607.

9. On or about May 27, 1981, the State filed an amended complaint, asserting claims under Section 7003 of RCRA, 42 U.S.C. § 6973, Section 107 of CERCLA, 42 U.S.C. § 9607, Minn. Stat §§ 115.061, 115.07, 115.071, and Minnesota Rule WPC 4(b) [Minn. Rule Part 7100.0020], and Minnesota common law.

10. On or about August 31, 1981, and October 16, 1981, respectively, St. Louis Park and Hopkins filed amended complaints alleging, inter alia, claims under Section 7003 of RCRA, 42 U.S.C. § 6973, Section 107 of CERCLA, 42 U.S.C. § 9607, Minn. Stat. Chapter 116B, and Minnesota common law.

11. On or about April 5, 1985, the Court granted the State's motion for leave to file a second amended complaint, adding claims under the Minnesota Environmental Response and Liability Act ("MERLA"), Minn. Stat. Ch. 115B. The State subsequently filed such a second amended complaint. Pursuant to stipulations, St. Louis Park and Hopkins later also filed second amended complaints, each of which added MERLA claims.

12. Reilly, in its answers to the various complaints referenced above, has denied and continues to deny liability, has raised several affirmative defenses, and has asserted a counterclaim against St. Louis Park. Various other Parties have asserted cross-claims, including a cross-claim by St. Louis Park against the State, a cross-claim of Oak Park Village

Associates against the Housing and Redevelopment Authority of St. Louis Park and a cross-claim of Philip's Investment Co. against Reilly.

13. Since 1969, a number of studies and/or reports, chemical analyses and field investigations relating to the Site have been undertaken. By listing the items below, the Parties do not necessarily endorse the accuracy, correctness, precision, quality, or validity of the information and opinions contained therein. These analyses, investigations and studies include but are not limited to the following:

(a) Studies and/or Reports

- (1) "Ground Water Investigation Program at St. Louis Park, MN," by E. A. Hickok & Associates, Inc., September, 1969.
- (2) "Memorandum of Waste Disposal at Republic Creosote Co. and Reilly Tar & Chemical Co.," by Minnesota Pollution Control Agency (MPCA Board Item), April, 22, 1970.
- (3) "An Assemblage of Analytical Data Regarding the Reilly Tar & Chemical Property, St. Louis Park, Minnesota," by the St. Louis Park Health Department, August 1, 1972.
- (4) "Status Report on Creosote Site and TexaTonka Area", prepared by the St. Louis Park Planning Department, January 11, 1973.
- (5) "Surface and Subsurface Ground Reclamation; Republic Creosote Site, City of St. Louis Park", prepared by OSM Consulting Engineers, April 23, 1973.

- (6) "Storm Water Study; Public Improvement #72--43 (Republic Creosote Area)," prepared by OSM Consulting Engineers, August 6, 1973.
- (7) "Geology of the St. Louis Park Area - A Review by the Minnesota Geological Survey; Report on Investigation of Municipal Water Supply, St. Louis Park," prepared by the Minnesota Department of Health, March 1974.
- (8) "Soil Investigation; Proposed Storm Sewer and Holding Ponds near Highway 7 and Louisiana Avenue, St. Louis Park," prepared by Soil Exploration Co., April 16, 1974.
- (9) "Hydrogeologic Study of the Republic Creosote Site," prepared by Gerald Sunde, Consulting Engineer, July, 1974.
- (10) "Report on Investigation of Phenol Problem in Private and Municipal Wells in St. Louis Park, Minnesota," prepared by Minnesota Department of Health, September, 1974.
- (11) Memorandum from F. F. Heisel, Minnesota Department of Health, to P. Gove, Minnesota Pollution Control Agency. "St. Louis Park Creosote Contamination Study," November 14, 1975.
- (12) "Data Regarding The History and Development of a Storm Sewer System for the City in the Area of the Former Republic Creosote Property," prepared by the City of St. Louis Park, November 15, 1974.
- (13) "Memorandum on Groundwater Contamination, St. Louis Park, MN," by Minnesota Pollution Control Agency, (MPCA Board Item) November 19, 1974.
- (14) "Memorandum on St. Louis Park Groundwater Situation," by the Minnesota Pollution Control Agency, (MPCA Board Item) December 13, 1974.

- (15) "Soil and Ground Water Investigation Coal Tar Distillation and Wood Preserving Site, St. Louis Park - Phase I Report," prepared by Barr Engineering Co., May 1976.
- (16) "Stability Study of Para Benzo Quinone for the City of St. Louis Park," prepared by Sanitary Engineering Laboratories Inc. (SERCO), June 1976.
- (17) "Soil Boring and Chemical Analysis of the Northern Portion of Oak Park Village," prepared by National Biocentric, Inc., September 17, 1976.
- (18) "Soil Contamination by Creosote Wastes," prepared by National Biocentric, Inc., November 1, 1976.
- (19) "Development Plan, Northern Portion, Oak Park Village," prepared by St. Louis Park, December 2, 1976.
- (20) "Review of Recent Studies of Soil Contamination at the Former Republic Creosote Site - Recommendations to City's Proposed Development Plan," by Minnesota Pollution Control Agency, December 28, 1976.
- (21) "Soil and Ground Water Investigation Coal Tar Distillation and Wood Preserving Site, St. Louis Park - Phase II Report," prepared by Barr Engineering Co., June 1977.
- (22) "Assessment of Possible Human Health Effects Resulting from Contamination of the Former Republic Creosote Site," prepared by the Minnesota Department of Health, October 1977.
- (23) "Soil Report; Prepared by Oak Park Village, St. Louis Park, Minnesota," prepared by Soil Testing Service of Minnesota, Inc., January 5, 1978.
- (24) "Recommendations for Plugging or Modification of Abandoned Wells in the

Area of the Former Republic Creosote Plant," prepared by the City of St. Louis Park, January 11, 1978.

- (25) "Report of Well Water Survey, St. Louis Park, Minnesota," prepared by Sanitary Engineering Laboratories, Inc., (SERCO) June-July 1978.**
- (26) "Report on the Existing Creosote Problem in St. Louis Park, Minnesota," prepared by James Bailey, Agricultural Engineering, University of Minnesota, July 1, 1978.**
- (27) "Health Implications of Polynuclear Aromatic Hydrocarbons in St. Louis Park Drinking Water," prepared by the Minnesota Department of Health, November 1978.**
- (28) "Status Report to the MPCA: Proposed Development, Oak Park Village," prepared by St. Louis Park, November 14, 1978.**
- (29) "Water Quality Development in Oak Park Village," prepared by St. Louis Park Planning Department, December 15, 1978.**
- (30) "Letter Report Tabulating Information on Existing Wells in St. Louis Park," prepared by United States Geological Survey, February 6, 1979.**
- (31) "Status Report: St. Louis Park Development," by the Minnesota Pollution Control Agency (MPCA Board Item), March 27, 1979.**
- (32) "Progress Report: Investigation of Coal Tar Derivatives in Ground Water - St. Louis Park," prepared by the United States Geological Survey, April 13, 1979.**
- (33) "Epidemiologic Investigation of Third National Cancer Survey Data for St. Louis Park, Edina, Richfield and Minneapolis St. Paul SMSA with a**

Historical Review of St. Louis Park's Water Supply," prepared by Kari Dusich, September 1979.

- (34) "Emergency Pumpout Well For Reilly Tar Site, St. Louis Park, Minnesota," prepared by Ecology and Environment, Inc., 1980.
- (35) "Examination of Cost Estimate For Three Tasks to be Completed For The Reilly Tar and Chemical Project, St. Louis Park, MN," prepared by Ecology and Environment, Inc., 1980.
- (36) "Summary Report on the City of St. Louis Park Activated Carbon Pilot Plant Study," prepared by Sanitary Engineering Laboratories, Inc., (SERCO), January 11, 1980.
- (37) "Cancer Rates in a Community Exposed to Low Levels of Creosote Components in Municipal Water," prepared by Dusich, Sigurdson, Hall, Dean, Minnesota Medicine, November 1980.
- (38) "Preliminary Evaluation of Ground Water: Contamination by Coal Tar Derivative, St. Louis Park, MN," prepared by the United States Geological Survey, January 1981.
- (39) "Report on Drinking Water Treatment and Remedy Evaluation for St. Louis Park, MN," prepared by Eugene A. Hickok and Associates, Inc., April 1981.
- (40) "Report and Statistic - Water Quality: Results of St. Louis Park Water Samples," prepared by H. Taylor, United States Geological Survey, June 10, 1981.
- (41) "Study of Ground Water Contamination in St. Louis Park, MN," prepared by Eugene A. Hickok & Associates, et. al., November 1981.
- (42) "Dispersion and Sorption of Hydrocarbons in Aquifer Material," by

G. Cohn (thesis) University of Minnesota, 1982.

- (43) "Terminating An Endless Search: An Action Approach to Solving the Water Problem," prepared by St. Louis Park, January 11, 1982.
- (44) "Request for Authorization to Negotiate and Enter into Cooperative Agreement with the U.S. EPA to Obtain Funds for Additional Cleanup Work at the Reilly Tar Site, St. Louis Park," by the Minnesota Pollution Control Agency (MPCA Board Item), May 25, 1982.
- (45) "Degradation of Phenolic Contaminants in Ground Water by Anaerobic Bacteria: St. Louis Park, MN," prepared by Erlich, Goerlitz, Godsy & Hult, United States Geological Survey, November 1982.
- (46) "Evaluation of Groundwater Treatment and Water Supply Alternatives for St. Louis Park, MN," prepared by CH2M Hill, 1982-1983.
- (47) "Recommended Plan for a Comprehensive Solution of the Polynuclear Aromatic Hydrocarbon Contamination Problem in the St. Louis Park Area," prepared by Environmental Research & Technology, Inc. for Reilly Tar & Chemical Corporation, April 1983, plus Errata, June 27, 1983 and November 27, 1984.
- (48) "Health Risk Assessment and Environmental Effects of Compounds Contaminating St. Louis Park Groundwater: Selected Two - and Three - Ring Heterocycles and Indene," prepared by Stephen M. Mabley, Minnesota Department of Health, Section of Health Risk Assessment, July 1983.
- (49) "Evaluation of Activated Carbon Treatment Alternative for Polynuclear Aromatic Hydrocarbon Removal for Groundwater in the St. Louis Park Area," prepared by Calgon Carbon Corporation, November 18, 1983.

- (50) "Request for Authorization to Negotiate and Execute an Amendment to the Current Cooperative Agreement with the U.S. Environmental Protection Agency for Investigation and Remedial Action at the Reilly Tar and Chemical Company Hazardous Waste Site in St. Louis Park," by the Minnesota Pollution Control Agency (MPCA Board Item), November 22, 1983.
- (51) "Assessment of Groundwater Contamination by Coal Tar Derivatives, St. Louis Park Area, MN", prepared by M. F. Hult, United States Geological Survey, Open File Report 84-867, 1984.
- (52) "Record of Decision, Remedial Action Alternative Selection," prepared by the United States Environmental Protection Agency, June 6, 1984.
- (53) "Evaluation of Granular Activated Carbon for the Removal of Polynuclear Aromatic Hydrocarbons from Municipal Well Water in St. Louis Park, MN," prepared by Calgon Carbon Corporation, September 10, 1984.
- (54) "Sampling and Analysis Plan for Calgon Accelerated Column Testing of SLP 15 Water," prepared by Environmental Research & Technology, Inc., October 25, 1984.
- (55) "Request for Issuance of a Request for Response Action to the Reilly Tar and Chemical Corporation Regarding Contamination At and Around the Reilly Tar Hazardous Waste Site in St. Louis Park," by the Minnesota Pollution Control Agency (MPCA Board Item), December 18, 1984.
- (56) "Ground-water Flow in Prairie du Chien Jordan Aquifer Related to Contamination by Coal Tar Derivatives, St. Louis Park, MN," prepared by J. R. Stark and M. F. Hult, United States Geological Survey, 1985.

- (57) "Calgon ACT Study: Initial Results from the Accelerated Column Test of PAH Removal Performance for Activated Carbon Treatment of Water From SLP 15," prepared by Twin City Testing, January 11, 1985.
- (58) "Calgon ACT Study: Further Results From the Study of PAH Removal by Activated Carbon Treatment," prepared by Twin City Testing, January 30, 1985.
- (59) "Keilly Tar and Chemical: Analysis of Water From Three St. Peter Wells," prepared by Twin City Testing, January 31, 1985.
- (60) "Accelerated Column Test for Removal of Polynuclear Aromatic Hydrocarbons from Contaminated Groundwater," prepared by Calgon Corporation, March 8, 1985.
- (61) "PAH Analysis by GCMS," prepared by Twin City Testing March 26, 1985
- (62) "Draft Work Plan R1, Reilly Tar Site, St. Louis Park, Minnesota," prepared by CH2M Hill and Ecology & Environment, April 27, 1985.
- (63) "Predesign Memorandum Evaluation of Granular Activated Carbon System Alternatives For Removal of Polynuclear Aromatic Hydrocarbons From Municipal Well Water in St. Louis Park, Minnesota", prepared by CH2M Hill, May 29, 1985.
- (64) "PAH Threshold Odor Determination in St. Louis Park Municipal Supply Water," prepared by Environmental Research and Technology, Inc., May 30, 1985.
- (65) "Volatile Organic Analysis of the St. Louis Park Municipal Drinking Water Supply System, March, 1985," prepared by Environmental Research & Technology, Inc., May 30, 1985.
- (66) "Feasibility of Community-Wide Epidemiologic Studies of Drinking Water and Health: St. Louis Park and New Brighton", prepared by the Minnesota Department of Health, December 31, 1985.

- (b) Field investigations and chemical analyses of water (surface and/or ground water) and soils, including associated field notes, chain of custody records, raw data sheets, sampling analysis protocols, boring and well logs and water level measurements. In general, the results of soil borings and water samples are found in the list of studies and/or reports under Part C. 13(a). (Dates listed usually reflect the time of the investigation.)
- (1) Preliminary soil investigation for the engineering properties of the soil, performed by Soil Engineering Services, Inc., October 13, 1969.
 - (2) Mellon-Rice data on well water and plant wastewater samples, Carnegie-Mellon University and C.W. Rice Division, NUS, November 5, 1970.
 - (3) Soil sample analyses, Tri-City Public Health Lab, 1971 and 1973.
 - (4) Analysis of soil and water samples from the St. Louis Park area, by the Minnesota Department of Health, 1973 to present.
 - (5) Analysis of soil and water samples by Twin Cities Testing and Engineering Laboratory, Inc., and Soil Exploration Company, 1974 to present.
 - (6) Analysis of soil and water samples by Sanitary Engineering Laboratories, Inc. (SERCO), 1975, 1976, 1977, 1978 and 1982.
 - (7) Soil borings performed by Braun Engineering, 1974, 1979, 1980, and 1982.
 - (8) Well investigations pursuant to well abandonment program performed by Minnesota Department of Health, 1978-present.
 - (9) Analysis of soil and water by United States Geological Survey, 1978-present.

- (10) Analyses of groundwater, by Pace Laboratories, Inc., 1978-1980, 1983-1984 (1983-1984 analyses performed by Rocky Mountain Analytical Laboratory).
- (11) "Results of Analysis of Water Samples, and Soil Samples for Polynuclear Aromatic Compounds (Hydrocarbons, Azarene, Phenols)", by Midwest Research Institute, October 7, 1981.
- (12) Analyses of Ground Water, by Capsule Laboratories, Inc., 1981, 1982, and 1983.
- (13) Soil borings and analyses by GCA Corp., 1982-1983.
- (14) Water analyses by Monsanto Research Corp., 1982-1984.
- (15) Water analyses by Environmental Testing and Certification Corporation, 1983.
- (16) Soil boring and chemical analyses by National Biocentric, Inc., 1976.
- (17) St. Louis Park area water well search and inventory questionnaires, prepared by E. A. Hickok and Associates, Inc., 1982-1983.
- (18) Progress reports on the investigation and clean-out of W23 and W105, E.A. Hickok & Associates, Inc., 1982 to present.
- (19) Water samples and analyses by CH2M Hill, 1982 and 1983.
- (20) Water samples and analyses by Environmental Research and Technology, Inc., 1982 to present.
- (21) Water samples and analyses by Acurex Corporation, 1984 to present.
- (22) Water analyses by United States Environmental Protection Agency 1977 and 1981-1982.



HEALTH AND SAFETY PLAN

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SECTION D
COMMUNITY RELATIONS PLAN

COMMUNITY RELATIONS PLAN

The Initial Sampling Plan is to be completed in accordance with the Consent Decree - Remedial Action Plan for Reilly Tar & Chemical Corporation's St. Louis Park, Minnesota, N.P.L. Site. All community relations programs related to this work will be coordinated through the following agencies:

United States

Ms. Judy Beck

**United States Environmental Protection Agency
(312) 353-1325**

State of Minnesota

Ms. Susan Brustman

**Minnesota Pollution Control Agency
(612) 296-7769**

City of St. Louis Park

Ms. Sharon Klumpp

**City of St. Louis Park
(612) 924-2523**

Information necessary to conduct the Community Relations Plan will be provided by the City and Reilly.